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ABSTRACT

Interlaboratory Proficiency Test 07/2017

Proftest SYKE arranged the proficiency test (PT) for measurement the gross and the net calorific value, the content of ash, carbon, nitrogen, hydrogen, moisture, sulphur and volatile matter in peat, wood pellet (not sulphur) and coal samples in September 2017. In total, there were 26 participants in the PT. Also, the participants had the possibility to calculate the emission factor for the peat and coal samples. In total, 89 % of the participants reported satisfactory results when the deviations of 1–30 % from the assigned values were accepted. In measurement of the gross calorific value from the peat sample 100 %, from the wood pellet sample 83 % and from the coal sample 94 % of the results were satisfactory. In measurement of the net calorific value from the peat sample 100 %, from the wood pellet 83 % and from the coal sample 92 % of the results were satisfactory.
The robust mean or mean of the reported results by the participants were used as the assigned values for measurements. The evaluation of performance was based on the z and E_n scores. The evaluation of performance was not done for the measurement of M_{ad} in all samples, H_d in the peat sample and N_d in the wood pellet sample.
Warm thanks to all the participants of this proficiency test!

Keywords: Proficiency test, interlaboratory comparison, coal, peat, wood pellet, calorific value, emission factor, ash, moisture, carbon, sulphur, nitrogen, hydrogen, volatile matter, environmental laboratories

TIIVISTELMÄ

Laboratorioiden välinen pätevyyskoe 07/2017

Proftest SYKE järjesti syyskuussa 2017 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin, haihtuvien yhdisteiden ja kosteuden määrittämiseksi turpeesta, puupelletistä (ei rikkiä) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus arvioida/laskea turve- ja kivihiilinäytteiden päästökerroin. Pätevyyskokeessa oli yhteensä 26 osallistujaa. Koko tulosaineistossa hyväksyttäviä tuloksia oli 89 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 100 % (turve), 83 % (puupelletti) ja 94 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 100 % (turve), 83 % (puupelletti) ja 92 % (kivihiili). Vertailuarvona käytettiin osallistujatulosten robustia keskiarvoa tai keskiarvoa. Pätevyyden arviointi tehtiin z- ja E_n -arvojen avulla.
Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, turpeen vedyn ja puupelletin typen määrityksille.
Kiitos pätevyyskokeen osallistujille!

Avainsanat: pätevyyskoe, vertailumittaus, kalorimetrinen lämpöarvo, tehollinen lämpöarvo, päästökerroin, tuhka, kosteus, hiili, rikki, typpi, haihtuvat yhdisteet ja vety, turve, puupelletti, hiili, ympäristölaboratoriot

SAMMANDRAG

Provningsjämförelse 07/2017

Proftest SYKE genomförde i september 2017 en provningsjämförelse som omfattade bestämningen av kalorimetriskt och effektivt värmevärde, svavel, väte, kol, kväve, askhalt, flykthalt och fukthalt i torv, träd pellet (inte svavel) och stenkol. Det var en möjlighet att beräkna emissionfaktor i torv och stenkol prover. Totalt 26 deltagarna deltog i jämförelsen.
Som referensvärde för analyternas koncentration användes mest det robusta medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z och E_n värden. I jämförelsen var 89 % av alla resultaten acceptabel, när en total deviation på 1–30 % från referensvärdet tilläts. Av det kalorimetriska värmevärdet var 100 % acceptabla (torv), 83 % (träd pellet) och 94 % (stenkol). För resultaten av det effektiva värmevärdet var 100 % (torv), 83 % (träd pellet) och 92 % (stenkol) acceptabla. Det var inte gjorts värdering till fuktighalt i alla prover, beräkning av väte i torv provet och nitrogen i träd pellet.
Ett varmt tack till alla deltagarna i testet!

Nyckelord: provningsjämförelse, kalorimetriskt och effektivt värmevärde, emissionfaktor, svavel, väte, kol, nitrogen, askhalt, flykthalt fukthalt stenkol, torv, träd pellet, miljölaboratorier

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of gross and net calorific value in fuels in September 2017 (CAL 07/2017). In total there were 26 participants in the PT. In the PT, gross and net calorific value, C_d, S_d, H_d, N_d, moisture content of the analysis sample ($M_{ad,d}$), ash content as well as volatile matter (V_{db}) were tested in peat, wood pellet (not S) and coal samples.

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability. The proficiency test was carried out in accordance with the international guidelines ISO/IEC17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service (FINAS) as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/sites/en). This proficiency test has been carried out under the accreditation scope of the Proftest SYKE.

2 Organizing the proficiency test

2.1 Responsibilities

Organizer:

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Ultramariinikuja 4 (formerly Hakuninmaantie 6), FI-00430 Helsinki, Finland
Phone: +358 295 251 000
E-mail: proftest@environment.fi

The responsibilities in organizing the proficiency test were as follows:

Mirja Leivuori	coordinator
Riitta Koivikko	substitute of coordinator
Keijo Tervonen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Co-operation:

Minna Rantanen from Eurofins Environment Testing Finland Oy (formerly Ramboll Finland Oy) was participating in organizing the proficiency test as well as acting analytical expert.

Subcontracting:
The peat, wood pellet and coal samples were homogenated and divided into sub-samples at the laboratory of Water Protection Association of the Kokemäenjoki River in Tampere (Finland, testing laboratory T064 accredited by FINAS, www.finas.fi/sites/en). Samples were tested by Eurofins Environment Testing Finland Oy (T039 accredited by FINAS, www.finas.fi/sites/en).

2.2 Participants

In total 26 participants took part in this proficiency test, of which 8 were from Finland and 18 from other countries (Appendix 1).

Altogether 77 % of the participants used accredited analytical methods at least for a part of the measurements. The samples were tested at the laboratory of Eurofins Environment Testing Finland Oy, Vantaa and their participant code is 18 in the result tables.

2.3 Samples and delivery

Three different fuel samples were delivered to the participants: peat (B1), wood pellet (B2) and coal (K1) samples. Gross ($q_{V,gr,d}$) and net ($q_{p,net,d}$) calorific value, C_d, S_d, H_d, N_d, moisture content of the analysis sample ($M_{ad,d}$), ash content as well as volatile matter (V_{db}) were tested in peat, wood pellet (not S) and coal samples.

The material for the peat sample (B1) was collected from the Finnish marshland. The material was air dried and grounded by the mill with 500 µm sieve before homogenization and sample dividing. The peat sample was prepared by Labtium in Jyväskylä (Finland).

The wood pellet sample (B2) was provided by Vapo and it was pre-treated (grinding) by Labtium. The raw material for wood pellets was spruce sawdust. The material was first crushed with a cutting mill and then grounded by the mill with 1000 µm sieve before homogenization and sample dividing.

The coal sample (K1) was prepared from hard coal by the Helen Ltd (Finland). All samples were homogenized and divided into sub-samples at the laboratory of Water Protection Association of the Kokemäenjoki River in Tampere. The sample preparation is described in details in the Appendix 2.

In the cover letter delivered with the samples, the participants were instructed first to store the samples closed for one day after their arrival and then to measure the moisture content of the analysis sample (M_{ad}) as the first measurement. The samples were instructed to be homogenized before measurements and to be stored in a dry place at room temperature. Further, the moisture content of the analysis sample was instructed to be measured on every day of measurements. This was important as it eliminates the influence of humidity on the measurements. The participants were also asked to report the relative humidity (%) of the measuring room as an average of the measuring dates.

Participants had the possibility to estimate/calculate the emission factor (as received), EF, for peat and coal samples. For this estimation/calculation the total moisture contents of the samples as received (M_{ar}) were given:

- peat B1 34.2 %,
- coal K1 9.6 %

The samples were delivered on 1 September 2017 to the participants. The samples arrived to the participants mainly latest on 8 September 2017.

The samples were requested to be measured and the results to be reported latest on 25 September 2017. Two participants delivered the results one day later. The preliminary results were delivered to the participants via ProftestWEB and email on 2 October 2017.

2.4 Homogeneity

Homogeneity of the samples B1, B2 and K1 was tested by measuring the gross calorific value and ash content as duplicate determinations from five subsamples (Appendix 3). Moreover, the other measurands were tested from two subsamples as duplicate measurements. According to the homogeneity test results, all samples were considered homogenous.

Particle size distribution was also tested from one sub sample of peat (B1) and coal (K1). The requirement of particle sizes given in the international standards was not totally fulfilled (Appendix 2). However, based on the results of this PT this seems not to have influenced the performance of the participants measuring the coal sample.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 4. The comments from the participants mainly dealt with sample delivery and participants' reporting errors. The comments from the provider are mainly focused to the lacking conversancy to the given information with the samples. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. Also before the statistical results handling some outliers were rejected in cases, where the result differed from the data more than $s_{rob} \times 5$ or 50 % from the robust mean or the result was reported erroneously (e.g. wrong unit). The rejection of results was partly based to the rather strict requirements for the reproducibility given in the standards for analysis described in the covering letter of the samples. The duplicate results were tested using the Cochran test. If the result was reported lower than detection limit, it has not been included in calculations.

More information about the statistical handling of the data is available in the Guide for participant [4].

2.6.2 Assigned values

Mainly the robust mean of the participants results was used as the assigned value for measurements of the test samples, when there were at least 12 results (n(stat)≥12). In calculation of the robust mean the outliers are normally not rejected, but they are iterated before the final calculation of the robust mean (Appendix 6). However, in this proficiency test some extreme results were considered as clear outliers and thus rejected. Also the mean and the median values of the data were calculated and they were quite similar to the assigned values (Table 1). In cases, where the number of results was lower than 12, the mean value of the participants results was used as the assigned value (the peat sample B1: all measurands; the sample B2: C_d, H_d, N_d, $q_{p,net,d}$, V_{dp}; the sample K1: H_d, N_d, V_{dp}).

Assigned value was given neither for analysis moisture content $M_{ad,d}$ (all samples) nor for hydrogen, H_d, in the peat sample (B1, high deviation of the results). For nitrogen, N_d, in the pellet sample (B2) the informative assigned value is given, but due to the high deviation of the results the performance evaluation was not done. In cases, where the number of results was less than 6 (n(stat)<6), the performance evaluation was done using E_n score, if the assigned value and its measurement uncertainty was set (C_d, EF, and N_d in the peat sample B1).

When the robust mean was used as the assigned value, the expanded measurement uncertainty was calculated using the robust standard deviation. When the mean value was used as the assigned value, the expanded measurement uncertainty was estimated based on the standard deviation [2, 4]. When using the robust mean or mean of the participant results as the assigned value, the standard uncertainties of the assigned values for calorific values were between 0.1 % and 0.4 %. For the other evaluated measurands the uncertainty varied from 0.4 % to 10 % (Appendix 5).

The participants also calculated emission factors (EF) for the peat (B1) and coal (K1) samples according to the given total moisture contents as received (M_{ar}). In this PT, very few participants reported their results for the emission factor (4-8). Due to the low number of the reported results the peat sample (B1) was evaluated based on E_n score.

The results for analysis moisture content ($M_{ad,d}$) have not been evaluated due to high deviation in the results, but the assigned values are shown. The results of nitrogen in the wood pellet sample have not been evaluated due to high deviation of the results and low concentration level, but the assigned values are shown (Table 1).

After reporting the preliminary results no changes have been done for the assigned values.

2.6.3 Standard deviation for proficiency assessment and results' evaluation

The requirements for the reproducibility of the used standard methods were reported in the cover letter of the samples and they were used for estimation of standard deviation for proficiency assessment in this PT. The reproducibility required for the standard methods was mainly fulfilled for gross calorific values. The standard deviation for the proficiency assessment ($2\times s_{pt}$ at the 95 % confidence level) was set to 1–30 % depending on the measurements. After reporting the preliminary results **no changes have been done for the standard deviations of the proficiency assessment values.**

Additionally, when the number of reported results was low and the uncertainty was set for the assigned value, and the participant reported measurement uncertainty, the performance was estimated by means of E_n scores ('*Error, normalized*', Appendix 9). These are used to evaluate the difference between the assigned value and participant's result within their claimed expanded uncertainty. E_n scores are calculated:

$$(E_n)_i = \frac{x_i - x_{pt}}{\sqrt{U_i^2 + U_{pt}^2}}, \text{ where}$$

x_i = participant's result, x_{pt} = assigned value, U_i = the expanded uncertainty of a participant's result and U_{pt} = the expanded uncertainty of the assigned value.

E_n scores of $-1.0 < E_n < 1.0$ should be taken as an indicator of successful performance when the uncertainties are valid. Whereas scores $E_n \geq 1.0$ or $E_n \leq -1.0$ could indicate a need to review the uncertainty estimates, or to correct a measurement issue.

The reliability of the assigned values was tested according to the criterion $u_{pt} / s_{pt} \leq 0.3$, where u_{pt} is the standard uncertainty of the assigned value and s_{pt} is the standard deviation for proficiency assessment [2, 3]. When testing these reliabilities the criterion was mainly fulfilled and the assigned values were considered reliable.

The reliability of the target value of the standard deviation and the corresponding z score was estimated by comparing the deviation for proficiency assessment (s_{pt}) with the robust standard deviation (s_{rob}) or standard deviation (sd) of the reported results [3]. The criterion s_{rob} (or sd)/ s_{pt} < 1.2 was mainly fulfilled.

In the following case, the criteria for the reliability of the assigned value and for the reliability of the target value for the deviation were not met and, therefore, the evaluation of the performance is reduced in this proficiency test:

Sample	Measurand
B1	Ash_d

3 Results and conclusions

3.1 Results

The summary of the results of this proficiency test is presented in Table 1. Explanations to terms used in the result tables are presented in Appendix 6.The results and the performance of each participant are presented in Appendix 7. The reported results with their expanded uncertainties (k=2) are presented in Appendix 8. The summaries of the z and E_n scores are shown in Appendix 9 and the z scores in the ascending order in Appendix 10.

The robust standard or standard deviations of the results varied from 0.3 to 30.7 % (Table 1). The robust standard or standard deviation was lower than 2 % for 52 % of the results and lower than 6 % for 87 % of the results (Table 1). For M_{ad} the robust standard deviation of the results was higher than 6 % (B1) and for N_d it was the highest 30.7 % (B2, Table 1). The robust standard or standard deviations were approximately within the same range as in the previous similar proficiency test Proftest SYKE 8/2016, where the deviations varied from 0.3 % to 59 % [5].

Table 1. The summary of the results in the proficiency test 07/2017.

Measurand	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2 x s_{pt} %	n (all)	Acc z %
Ash_d	B1	w%	3.14	3.14	3.14	3.16	0.17	5.4	8	11	100
	B2	w%	0.27	0.27	0.27	0.28	0.04	15.4	30	16	88
	K1	w%	11.0	11.1	11.0	11.0	0.1	0.8	2.5	18	94
C_d	B1	w%	55.4	55.4		55.3			-	5	-
	B2	w%	50.8	50.8	50.8	50.9	0.6	1.1	2.5	12	75
	K1	w%	71.9	72.0	71.9	71.8	0.8	1.1	2.5	15	87
EF	B1	t CO2/TJ	102	102		102			-	4	-
	K1	t CO2/TJ	93.6	93.6	93.6	93.6	0.9	1.0	4	8	100
H_d	B1	w%		5.95		5.87			-	5	-
	B2	w%	6.04	6.04	6.06	6.04	0.08	1.3	6	11	91
	K1	w%	4.69	4.69	4.69	4.66	0.14	3.0	6	13	85
$M_{ad,d}$	B1	w%	6.17	6.17	6.19	6.25	0.43	7.0	-	11	-
	B2	w%	8.26	8.24	8.26	8.30	0.30	3.7	-	19	-
	K1	w%	4.36	4.41	4.36	4.39	0.18	4.2	-	19	-
N_d	B1	w%	1.75	1.75		1.76			-	5	-
	B2	w%	0.076	0.076	0.076	0.072	0.023	30.7	-	10	-
	K1	w%	2.21	2.21	2.19	2.22	0.09	4.2	10	10	90
$q_{p,net,d}$	B1	J/g	21189	21189		21147			1.5	6	100
	B2	J/g	18881	18881	18861	18876	59	0.3	1.7	12	83
	K1	J/g	28343	28343	28343	28330	126	0.4	1.1	13	92
$q_{V,gr,d}$	B1	J/g	22408	22408	22416	22400	131	0.6	1.3	10	100
	B2	J/g	20170	20161	20170	20224	130	0.6	1.5	18	83
	K1	J/g	29342	29343	29342	29339	100	0.3	1.0	18	94
S_d	B1	w%	0.20	0.20	0.20	0.20	0.01	5.5	15	7	100
	K1	w%	0.35	0.35	0.35	0.35	0.02	6.7	15	16	88
V_{db}	B1	w%	69.7	69.7	69.7	69.6	0.9	1.2	3	7	100
	B2	w%	85.0	85.0	85.1	85.1	0.6	0.7	3	8	88
	K1	w%	35.5	35.5	35.1	35.5	1.0	2.7	3	13	62

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, $2\times s_{pt}$ %: the standard deviation for proficiency assessment at the 95 % confidence level, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

In this proficiency test the participants were requested to report replicate results for all measurements. The results of the replicate determinations based on the ANOVA statistics are presented in Table 2. The international standards or technical specifications related to the measurements of fuels, recommend the targets for the repeatability.

In particular, in measurements of the calorific values, the requirement for the repeatability is ± 120 J/g. In this proficiency test the requirements for the repeatability of the measurements of the gross calorific value were 0.54 % for the sample B1, 0.59 % for the sample B2 and 0.41 % for the sample K1 and in measurement of the net calorific value 0.57 %, 0.64 % and 0.42 %, respectively. In each case, the obtained repeatability of the measurement of the gross calorific value and the net calorific value was lower than the repeatability requirement (Table 2, the column s_w %).

Table 2. The summary of repeatability on the basis of replicate determinations (ANOVA statistics).

Measurand	Sample	Unit	Assigned value	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
Ash_d	B1	w%	3.14	3.14	0.038	0.147	0.152	1.2	4.7	4.8	3.9
	B2	w%	0.27	0.27	0.034	0.034	0.048	13	13	18	1.0
	K1	w%	11.0	11.1	0.055	0.153	0.162	0.50	1.4	1.5	2.8
C_d	B1	w%	55.4	55.4	0.063	0.381	0.386	0.11	0.69	0.70	6.0
	B2	w%	50.8	50.8	0.180	0.701	0.723	0.35	1.4	1.4	3.9
	K1	w%	71.9	72.0	0.139	0.899	0.910	0.19	1.2	1.3	6.5
EF	B1	t CO2/TJ	102	102	0.159	0.543	0.565	0.16	0.53	0.55	3.4
	K1	t CO2/TJ	93.6	93.6	0.107	0.944	0.950	0.11	1.0	1.0	8.8
H_d	B1	w%		5.95	0.047	0.184	0.190	0.79	3.1	3.2	3.9
	B2	w%	6.04	6.04	0.039	0.124	0.130	0.64	2.0	2.1	3.2
	K1	w%	4.69	4.69	0.026	0.124	0.127	0.54	2.7	2.7	4.9
$M_{ad,d}$	B1	w%	6.17	6.17	0.049	0.428	0.431	0.79	6.9	7.0	8.8
	B2	w%	8.26	8.24	0.033	0.333	0.335	0.41	4.0	4.1	10.0
	K1	w%	4.36	4.41	0.059	0.288	0.294	1.4	6.7	6.8	4.9
N_d	B1	w%	1.75	1.75	0.022	0.078	0.081	1.3	4.4	4.6	3.5
	B2	w%	0.076	0.076	0.007	0.020	0.021	8.9	26	28	3.0
	K1	w%	2.21	2.21	0.077	0.096	0.123	3.5	4.4	5.6	1.3
$q_{p,net,d}$	B1	J/g	21189	21189	23.1	100	103	0.11	0.47	0.49	4.3
	B2	J/g	18881	18881	37.3	126	132	0.20	0.67	0.70	3.4
	K1	J/g	28343	28343	36.3	117	123	0.13	0.41	0.43	3.2
$q_{V,gr,d}$	B1	J/g	22408	22408	20.2	131	133	0.090	0.59	0.59	6.5
	B2	J/g	20170	20161	42.3	149	155	0.21	0.74	0.77	3.5
	K1	J/g	29342	29343	38.0	85.2	93.3	0.13	0.29	0.32	2.2
S_d	B1	w%	0.20	0.20	0.0090	0.0088	0.013	4.6	4.5	6.4	0.98
	K1	w%	0.35	0.35	0.0076	0.024	0.025	2.2	6.8	7.2	3.1
V_{db}	B1	w%	69.7	69.7	0.087	0.748	0.753	0.13	1.1	1.1	8.6
	B2	w%	85.0	85.0	0.373	0.793	0.877	0.44	0.93	1.0	2.1
	K1	w%	35.5	35.5	0.145	1.05	1.06	0.41	3.0	3.0	7.2

Ass.val.: assigned value; s_w**:** repeatability standard error; s_b**:** between participants standard error; s_t**:** reproducibility standard error.

The estimation of the robustness of the methods could be done by the ratio s_b/s_w. The ratio s_b/s_w should not exceed the value 3 for robust methods. Here, however, the robustness exceeded the value 3 in many cases (Table 2). For the gross calorific value, the ratio s_b/s_w, was 6.5 (the sample B1), 3.5 (the sample B2) and 2.2 (the sample K1), for the net calorific values 4.3, 3.4 and 3.2, respectively. For the calorific values the ratio s_b/s_w was mainly within the same range than in the previous similar proficiency test CAL 08/2016, with the exception of somewhat higher ratio for the gross calorific value in the coal sample (K1) [5].

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. A questionnaire of some detailed information related to the used analytical methods was provided along the proficiency test. The summary of the answers is shown in Appendix 11. The used analytical methods and the results of the participants grouped by methods are shown in more detail in Appendix 12. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. However, in this PT there were not enough results for statistical comparison. Thus, the comparison is based on the graphical result evaluation.

3.2.1 Gross and net calorific value

The analytical methods based on different standard methods were used for the measurements in the proficiency test. The used analytical methods of the participants are shown in more detail in Appendix 12.

Mostly, standard methods were used for measurement of calorific value (EN 14918 [6], ISO 1928 [7], Appendix 11). Two participants used other standard (EN 15400, participants 9, 17) and one reported to used isoperibolic calorimeter (participant 12).

In the calculations of gross calorific value ($q_{V,gr,d}$), various correction factors were used. Fuse wire, ignition, acid, moisture, nitrogen and sulphur corrections were most commonly used in several different combinations depending of the test material (Appendix 11). For the calculation of net calorific value ($q_{p,net,d}$), different combinations of correction factors were used as well depending of the test material (Appendix 11). Mainly nitrogen plus oxygen (N+O) and hydrogen (H) content was used for corrections. Based on the graphical result evaluation, clear differences between the used methods in gross and net calorific value measurements could not be concluded.

3.2.2 Measurement of carbon, hydrogen, nitrogen, sulphur, moisture, ash and volatile matter

In the proficiency test the following several standard methods or technical specifications were mainly used for measurements of different parameters:

Measurand	Method
C, H and N	ISO 29541 [8], ASTM D 5373 [9], EN ISO 16948 [10]
S	ISO 334 [11], EN ISO 16994 [12], ASTM D 4239 [13]
Analytical moisture content	EN 14774-3 [14], ISO 589 [15], DIN 51718 [16], ASTM D 7582 [17], ASTM D 5142 [18], EN ISO 18134 [19], ISO 11722 [20]
Ash content	EN 14775 [21], ISO 1171 [22], ASTM D 7582 [17], ASTM D 5142 [18], EN ISO 18122 [23]
Volatile matter	EN 15148 [24], ISO 562 [25], EN ISO 18123 [26]

However, in some cases also other international and national standards or technical specifications (e.g. ISO 19579, EN 15403, CEN/TS 15414-3) or internal methods (e.g. participants 1, 6, 10-13, 16, 17, 21) were used. Moisture content was mainly determined gravimetrically by heating in air or N_2 atmosphere at the temperatures of 105-108 °C. Moisture content was measured also using TGA at the temperatures of 105 °C. Air and N_2 atmosphere was used for determining moisture content for coal samples. One participant used nitrogen atmosphere for the peat and wood pellet sample (Appendix 11).

The ash content was determined mainly gravimetrically by heating at the temperature 550 °C or 815 °C (Samples B1, B2) or at the temperature 815 °C (Sample K1). Ash content was measured also using TGA for samples at the temperatures between 550 °C and 815 °C (Appendix 11). In the international standards EN 14775 [21] and EN ISO 18122 [23] the ashing temperature is mentioned to be 550 °C and in ISO 1711 [22] it is mentioned to be 815 °C. Based on the graphical result evaluation, clear differences between the used methods in measurements could not be concluded.

Most of the participants conducted CHN analyses from air dried samples, and from dried samples one participant for the sample B1, four participants for the sample B2 and three participants for the sample K1 (Appendix 11). In the proficiency test also information of detection limit of nitrogen and sulphur was collected (Appendix 11).

3.3 Uncertainties of the results

At maximum 54 % of the participants reported the expanded uncertainties (k=2) with their results for at least some of their results (Table 3, Appendix 13). The range of the reported uncertainties varied between the measurements and the sample types.

Several approaches were used for estimating of measurement uncertainty (Appendix 13). The most used approach was based on method validation data. Two participants reported the usage of the MUkit measurement uncertainty software for the estimation of their uncertainties [27].

The free software is available in the webpage: www.syke.fi/envical/en. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 3. The range of the expanded measurement uncertainties (k=2, U_i%) reported by the participants.

Measurement	Uncertainty B1,%	Uncertainty B2, %	Uncertainty K1, %
Ash_d	2.8-10	0.2-34	0.3-10.5
C_d	1-3	1-40	0.3-5.5
EF	3-10	-	2-6.2
H_d	2-9	0.55-11	0.09-9
N_d	7-15	6.5-30	0.05-16
$q_{p,net,d}$	1-4	0.88-140	0.13-120
$q_{V,gr,d}$	0.46-2.1	0.7-140	0.13-120
S_d	8-14	-	0.01-14
V_{db}	1.4-5	1.4-10	0.26-5

The estimated uncertainties varied highly for all the tested measurements (Table 3). Especially, very low or high uncertainties can be considered questionable. It was evident, that some uncertainties had been reported erroneously for the measurands (including calorific values, Appendix 13), not as relative values as the provider of this proficiency test had requested. It is evident that the harmonization is still needed for the estimation of the expanded measurement uncertainties.

3.4 Estimation of emission factor

Additionally, the participants were asked to estimate the emission factors for the peat and coal samples distributed in the proficiency test by taking into account their own net calorific values and the total moisture values as received, which was informed in the cover letter of the samples. The calculation of the emission factor of the wood pellet sample (B2) was not done as it is a CO_2 neutral fuel. In this PT, very few participants reported their results for the emission factor (4-8). Due to the low number of the reported results, the peat sample (B1) was evaluated based on E_n score (Appendix 9).

4 Evaluation of the results

The evaluation of participants was based on the z scores and E_n scores, which were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory
$-1.0 < E_n < 1.0$	Satisfactory
$E_n \leq -1.0$ or $E_n \geq 1.0$	Unsatisfactory

Table 4. Summary of the performance evaluation in the proficiency test 07/2017.

Sample	Satisfactory results (%)	Accepted deviation from the assigned value (%)	Remarks
Peat, B1	100	1.3-15	• Very good performance. • Only approximate assessment for Ash_d. • In the CAL 08/16 the performance was satisfactory for 82 % of the results [5].
Wood pellet, B2	85	1.5-30	• Difficulties in measurements for C_d, < 80% satisfactory results. • In the CAL 08/16 the performance was satisfactory for 85 % of the results [5].
Coal, K1	88	1-15	• Difficulties in measurements for V_{db}, < 80% satisfactory results. • In the CAL 08/16 the performance was satisfactory for 91 % of the results [5].

In total, 89 % of the results evaluated based on z scores were satisfactory (Appendix 9) when accepting deviation of 1–30 % from the assigned value. All results evaluated based on E_n scores were satisfactory (Appendix 9). About 77 % of the participants used the accredited methods and 93 % of their results were satisfactory. In the previous similar proficiency test CAL 08/2016 the performance was satisfactory for 90 % of the results when deviation 1–30 % from the assigned value was accepted [5].

The summary of the performance evaluation is shown in Table 4. The percentage of the satisfactory results varied between 85 % and 100 % for the tested sample types. The criteria for performance had been mainly set according to the target value for reproducibility recommended in international standards or technical specifications for measurement of the calorific values and other determinants. The reproducibility required in the standards was fulfilled for the gross calorific values. For the net calorific value increased reproducibility from the value for the gross caloric value was used. There was no criterion for reproducibility for the net calorific value in standards methods.

Peat

In the previous similar proficiency test CAL 08/2016 the satisfactory results of the peat sample (B1) were in total 82 % [5], thus the performance in this PT is much better than previous (100 %, Table 4). The number of satisfactory results of the gross and net calorific values for wood pellet was higher for the gross calorific value and the net calorific value than in the previous proficiency test CAL 08/16 (82 % and 93 % respectively) [5]. The results of analysis moisture (M_{ad}) have not been evaluated, but the assigned values are presented (Table 1). The results of C_d, EF, N_d were evaluated based on the E_n scores, which were all satisfactory (Appendix 9).

Wood pellet

In the previous similar proficiency test CAL 08/2016 the satisfactory results of the wood pellet sample (B2) were in total 85 % [5], thus the performance in this proficiency test was the same (Table 4). The satisfactory results varied between 75 % (C_d) and 91 % (H_d) for the wood pellet

sample (Table 1). In the measurement of gross and net calorific values 83 % of the results were satisfactory when accepting deviations of 1.5 % and 1.7 % from the assigned values (Table 1). The number of satisfactory results of the gross and net calorific values for wood pellet was higher for gross calorific value and somewhat lower for the net calorific value than in the previous proficiency test CAL 08/16 (75 % and 86 % respectively) [5]. The estimation of EF was not done as it is a CO_2 neutral fuel. Also the results of analysis moisture (M_{ad}) and nitrogen (N_d) have not been evaluated, but the assigned value is given (Table 1).

Coal

In the previous similar proficiency test CAL 08/2016 the satisfactory results of the coal sample (K1) were in total 91 % [5], thus the performance was somewhat lower in this PT (88 %, Table 4). In the measurement of gross and net calorific values, 94 % and 92 % of results, respectively, were satisfactory, when accepting the deviations of 1 and 1.1 % from the assigned values (Table 1). The calculated emission factor results were all satisfactory. In this proficiency test the number of satisfactory result of the gross and net calorific values were higher than in the previous test CAL 08/16 (85 % and 84 %, respectively) [5]. The results of analysis moisture (M_{ad}) have not been evaluated, but the assigned value is given (Table 1).

5 Summary

Proftest SYKE carried out the proficiency test (PT) for the analysis of the gross and the net calorific value as well as for content of ash, carbon, hydrogen, nitrogen, sulphur, analytical moisture content and volatile matter in fuels in September 2017. Three types of samples were delivered to the participants: peat, wood pellet (not sulphur) and coal. In total 26 participants took part in the PT. Additionally, the participants were asked to estimate or calculate the emission factor for peat and coal samples.

The robust means (or means, n<12) of the results reported by the participants were used as the assigned values for measurements. The uncertainty for the assigned value was estimated at the 95 % confidence interval and it was less than 0.5 % for calorific values and at maximum 10 % for the other measurements.

The evaluation of the performance was based on the z scores, which were calculated using the standard deviation for proficiency assessment at 95 % confidence level. In cases where the number of the results was low, the performance was estimated by using E_n scores (C_d, EF, N_d in the peat sample). The evaluation of performance was not done for the measurement of M_{ad} in all samples, H_d in the peat sample and N_d in the wood pellet sample. In this proficiency test 89 % of the data was regarded to be satisfactory when the result was accepted to deviate from the assigned value from 1 to 30 %. About 77 % of the participants used accredited methods and 93 % of their results were satisfactory. In measurements of the gross calorific value from peat, wood pellet and coal samples, 100 %, 83 % and 94 % of the results were satisfactory, respectively. In measurements of the net calorific value from the peat, wood pellet and coal samples, 100 %, 83 % and 92 % of the results were satisfactory, respectively. In general, the

results were in the same range as in the previous similar Proftest SYKE proficiency test in CAL 08/2016 [5], but the performance in the gross calorific value was higher for peat, wood pellet and coal samples and also for the net calorific value for peat and coal samples in the present PT. For wood pellet sample the performance of the net calorific was somewhat lower in the present PT. The evaluation of data based on E_n scores show satisfactory performance for all results.

6 Summary in Finnish

Proftest SYKE järjesti syyskuussa 2017 pätevyyskokeen kalorimetrisen ja tehollisen lämpöarvon sekä tuhkan, vedyn, typen, rikin, kosteuden ja haihtuvien yhdisteiden määrittämiseksi turpeesta, puupelletistä (ei rikkiä) ja kivihiilestä. Lisäksi osallistujilla oli mahdollisuus laskea päästökerroin turve- ja kivihiilinäytteistä.

Pätevyyskokeeseen osallistui yhteensä 26 laboratoriota. Osallistujien pätevyyden arviointi tehtiin z-arvon avulla ja sen laskemisessa käytetyn kokonaishajonnan tavoitearvot olivat määrityksestä riippuen välillä 1–30 %. Turvenäytteen hiili, typpi ja päästökerroin arvioitiin käyttäen E_n-arvoa tulosten vähyyden vuoksi. Testisuureen vertailuarvona käytettiin osallistujien ilmoittamien tulosten robustia keskiarvoa tai keskiarvoa, jos tuloksia oli vähän ($n<12$). Tavoitearvon epävarmuus oli lämpöarvomäärityksissä alhaisempi kuin 0,5 % ja muiden määritysten osalta korkeintaan 10 %. Tulosten arviointia ei tehty testinäytteiden kosteuspitoisuuden määritykselle, vedyn määritykselle turpeesta ja typen määritykselle puupelletistä.

Koko tulosaineistossa hyväksyttäviä tuloksia oli 89 %, kun vertailuarvosta sallittiin 1–30 % poikkeama. Noin 77 % osallistujista käytti akkreditoituja määritysmenetelmiä ja näistä tuloksista oli hyväksyttäviä 93 %. Kalorimetrisen lämpöarvon tuloksista oli hyväksyttäviä 100 % (turve), 83 % (puupelletti) ja 94 % (kivihiili). Tehollisen lämpöarvon tuloksille vastaavat hyväksyttävien tulosten osuudet olivat 100 % (turve), 83 % (puupelletti) ja 92 % (kivihiili). Hyväksyttäviä tuloksia oli lähes saman verran kuin edellisessä vastaavassa pätevyyskokeessa CAL 08/2016 [5]. Turve-, pelletti- ja hiilinäytteiden osalta kalorimetrisen lämpöarvon sekä turve- ja hiilinäytteiden osalta tehollisen lämpöarvon määrityksissä menestyminen oli parempaa kuin edellisellä kierroksella. Pellettinäytteen osalta tehollisen lämpöarvon määrityksessä menestyminen oli jonkin verran heikompaa kuin edellisellä kierroksella. E_n-arvolla arvioidut tulokset olivat kaikki hyväksyttäviä.

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APPENDIX 1: Participants in the proficiency test

Country	Institute
Bulgary	AES-3C Maritza East 1 EOOD; Testing Laboratory "Energy Materials"
Estonia	Enefit Energiatootmine AS Chemical Laboratory
Finland	Ahma ympäristö Oy, Oulu
	Eurofins Environment Testing Finland Oy, Vantaa, Industry and Power Plant Chemistry
	Finnsementti Oy
	Fortum Waste Solutions Oy, Riihimäki
	Kymen Ympäristölaboratorio Oy
	Kymenlaakson ammattikorkeakoulu
	Labtium Oy, Jyväskylä
	Luonnonvarakeskus Kokkolan laboratorio
France	ArcelorMittal Fos sur Mer
	SOCOR Dechy France
Lithuania	AB "Siauliu Energija" chemijos laboratorija, Siauliai, Lithuania
Republic of Ireland	Edenderry Power Ltd
Republic of Korea	Komipo, Boryeong Thermal Power Site Division
	The Foundation of Agr. Tech. Commercialization and Transfer
Romania	Air Pollution Laboratory- INCD ECOIND- Bucuresti- Romania
	Ceprocim S.A. Romania
	CRH Ciment (Romania)-Punct de lucru Hoghiz
	Holcim Romania - Ciment Alesd
	Holcim(Romania) SA Ciment Campulung
	INCDE ICEMENERG Bucharest, National Research and Development Institute for Energy
	Laborator analize fizico-chimice apa si carbune, Romania
	ROMPETROL QUALITY CONTROL SRL-Laborator Produse Petroliere
Spain	Laboratorio Central de Calidad - LCC
Sweden	RISE Research Institutes of Sweden AB

APPENDIX 2: Preparation of the samples

Sample B1, peat

Sample B1 was prepared from peat taken from Finnish marshland.

The peat was air-dried (35 ºC) and grounded in a mill with a 500 µm sieve at the laboratory of Labtium. The dried and sieved sample was mixed by a mechanized sample mixer and distributed to sub-samples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of Water Protection Association of the Kokemäenjoki River. The particle size distribution of peat was measured by the laboratory of Labtium using laser diffraction (Malvern).

Sample B2, wood pellet

The sample B2 was provided by Vapo and it was prepared from spruce sawdust. The wood pellets were first crushed with a cutting mill and then grounded by the mill with 1000 µm sieve at the laboratory of Labtium. The sieved sample was mixed by a mechanized sample mixer and distributed to subsamples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory of Water Protection Association of the Kokemäenjoki River.

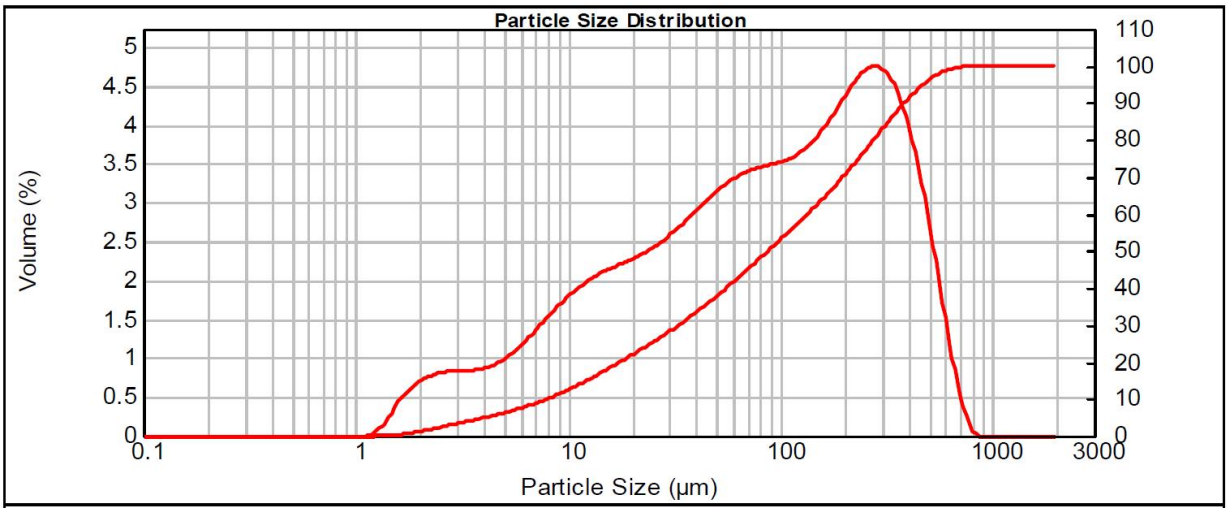
Sample K1, coal

Sample K1 was hard coal. The coal was dried at room temperature and grounded to particle size < 212 µm at the Helen Ltd. The dried and sieved sample was mixed by a mechanized sample mixer and distributed into subsamples of ca. 30 g using a rotary sample divider equipped with a vibratory sample feeder at the laboratory the laboratory of Water Protection Association of the Kokemäenjoki River. The particle size distribution of coal was measured by the Helen Ltd using laser diffraction (Malvern).

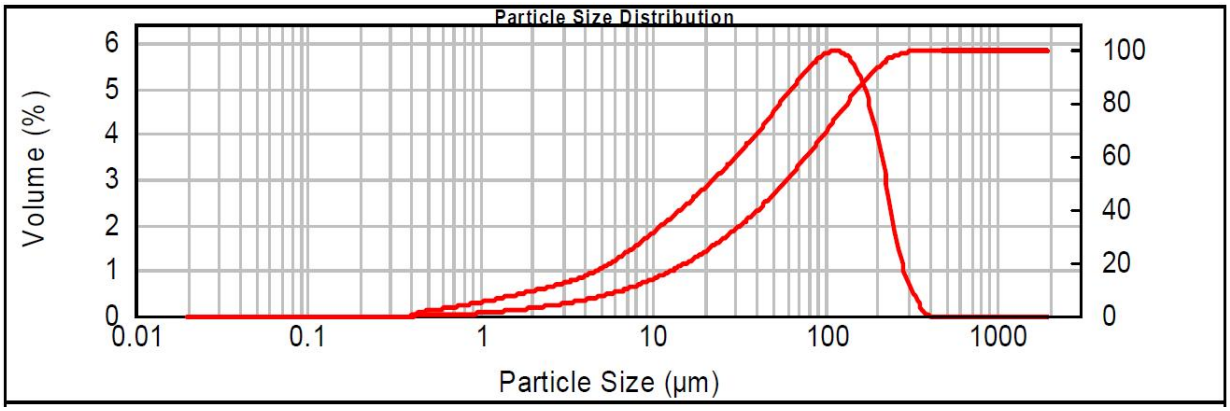
Particle size

To test the particle size of peat (B1) and coal (K1) samples tested using laser diffraction (Malvern).

Figure 1 is showing the distribution of particle size for the samples B1 and K1. For peat sample B1 the mean size of particles was 87 µm and ca. 98 % of the particles were smaller than 550 µm. For coal sample K1 the mean size of particles was 57.8 µm and 94.9 % of the particles were smaller than 212 µm. The requirements of particle sizes given in the international standards were not totally fulfilled for the tested material [6, 7]. However, based on the results of the PT this seemed not to have influenced the performance of the participants.



a) The particle size distribution of peat B1.



b) The particle size distribution of coal K1.

Figure 1. The particle size distribution of the fuel samples a) the peat (B1) and b) the coal (K1) sample.

APPENDIX 3: Homogeneity of the samples

Homogeneity was tested from duplicate measurements of calorific value (Table 1) and ash content in five samples, which were homogenised before sampling. Additionally, the other measurands from two samples was tested.

Criteria for homogeneity:

$s_{anal}/s_h<0.5$ and $s_{sam}^2<c$, where

s_h % = standard deviation for testing of homogeneity
s_{anal} = analytical deviation, standard deviation of the results within sub samples
s_{pt}% = standard deviation for proficiency assessment
s_{sam} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \times s_{all}^2 + F2 \times s_{anal}^2$, where
$s_{all}^2 = (0.3 \times s_h)^2$,
F1 and F2 are constants of F distribution derived from the standard statistical tables for the tested number of samples [2, 3].

Table 1. Results from the homogeneity testing for the calorific values of the peat (B1), pellet (B2) and coal (K1) samples.

Measurements	Mean	s_h%	s_{pt}%	s_h	s_{anal}	s_{anal}/s_h	Is $s_{anal}/s_h<0.5$?	s_{sam}	s_{sam}^2	c	Is $s_{sam}^2<c$?
Peat (B1)											
Gross calorific value, J/g	22399	0.5	0.65	112	54.3	0.48	yes	49.4	2440	8850	yes
Net calorific value, J/g	21033	0.75	0.75	158	54.3	0.34	yes	49.4	2440	11500	yes
Pellet (B2)											
Gross calorific value, J/g	20221	0.3	0.75	60.7	23.3	0.38	yes	28.2	800	1880	yes
Net calorific value, J/g	18815	0.3	0.85	56.4	23.3	0.41	yes	28.2	800	1770	yes
Coal (K1)											
Gross calorific value, J/g	29536	0.2	0.5	59.1	26.2	0.44	yes	19.4	380	2180	yes
Net calorific value, J/g	28523	0.2	0.55	57.0	26.2	0.46	yes	19.4	400	2130	yes

Conclusion: In each case, the criteria were fulfilled. **Thus, all the samples could be regarded as homogenous.** Also the results of the other tested measurands confirm the homogenous.

APPENDIX 4: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest
7, 9, 18	The samples were not delivered directly to the recipients, but to the delivery center by the distributor (Posti)	The provider used the standard postal parcel service instead of an express service. The provider regrets this situation, and seeks to avoid a similar kind of situation in the future.
10	The participant informed that they did not receive the preliminary results.	The preliminary results were delivered to the participants via email on 2nd October, 2017. The report of the preliminary results was also uploaded into the electronic client interface, ProftestWEB, on the same day.
14	The participants informed that the coal sample K1 was coarse and needed for further grinding.	The grain size distribution of the sample was measured and the sample did not totally fulfill the requirement of standards. Based on the participants' results the coarseness of the sample did not affect to the results.
All	The sample arrival form was not available from the electronic client interface, ProftestWEB, after sample delivery.	The provider attached the sample arrival form immediately after the note. The provider regrets the situation and seeks to avoid similar kind of situation in the future.

Participant	Comments to the results	Action / Proftest
6	The participants informed that they reported some results erroneously for coal sample (K1). The corrected results were: H_d: 4.75 and 4.74 w% V_{dp}: 34.86 and 34.77 w% Also they reported sulphur results for coal after reporting the preliminary results S_d: 0.32 and 0.32 w%	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the hydrogen and volatile organic compounds results had been reported correctly, the results for would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].
8	The participants informed that they reported some results erroneously for coal sample (K1). The corrected results were: $q_{p,net,d}$: 27017.42 J/g $q_{V,gr,d}$: 27842.23 J/g	The results were outliers in the statistical treatment, and thus did not affect the performance evaluation. If the results had been reported correctly, the results would have been satisfactory. The participant can re-calculate the z scores according to the Guide for participants [4].
14	The participants informed that they reported some results erroneously for peat sample (B1). The corrected results were: H_d: 5.815 and 5.905 w%	The hydrogen results were not evaluated for the peat sample.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
8	The participant reported only one result instead of replicate results for the measurands. The results have been excluded from the calculation of the assigned values. The participant did not report the used methods for some measurands, and provider added "Other method" to them due to the data handling process. The participant should follow more carefully the instructions given by the provider. In the future PTs no performance evaluation will be given for those results, which missed replicate results.
1, 4, 13	The participant did not report the used methods for some measurands, and provider added "Other method" to them due to the data handling process. The participants should follow more carefully the instructions given by the provider.
1, 4, 12, 13, 15, 17, 18, 26	For these participants the deviation of replicate measurements for some measurands and samples were high and their results were Cochran outliers. The provider recommends the participants to validate their deviation of replicate measurements.
All	It was evident, that some uncertainties had been reported erroneously for the measurands (including calorific values), not as relative values as the provider of this proficiency test had requested. The provider recommends the participants to validate the calculation of measurement uncertainties and follow more carefully the instructions given by the provider.

APPENDIX 5: Evaluation of the assigned values and their uncertainties

Measurand	Sample	Unit	Assigned value	U_{pt}	U_{pt}, %	Evaluation method of assigned value	u_{pt}/s_{pt}
Ash_d	B1	w%	3.14	0.09	2.9	Mean	0.36
	B2	w%	0.27	0.03	10.0	Robust mean	0.33
	K1	w%	11.0	0.1	0.5	Robust mean	0.20
C_d	B1	w%	55.4	0.3	0.6	Mean	
	B2	w%	50.8	0.4	0.8	Mean	0.32
	K1	w%	71.9	0.5	0.7	Robust mean	0.28
EF	B1	t CO2/TJ	102	1	0.5	Mean	
	K1	t CO2/TJ	93.6	0.7	0.7	Mean	0.18
H_d	B1	w%				Mean	
	B2	w%	6.04	0.03	0.5	Mean	0.08
	K1	w%	4.69	0.08	1.6	Mean	0.27
$M_{ad,d}$	B1	w%	6.17			Mean	
	B2	w%	8.26			Robust mean	
	K1	w%	4.36			Robust mean	
N_d	B1	w%	1.75	0.07	4.1	Mean	
	B2	w%	0.076			Mean	
	K1	w%	2.21	0.05	2.1	Mean	0.21
$q_{p,net,d}$	B1	J/g	21189	85	0.4	Mean	0.27
	B2	J/g	18881	19	0.1	Mean	0.06
	K1	J/g	28343	85	0.3	Robust mean	0.27
$q_{V,gr,d}$	B1	J/g	22408	90	0.4	Mean	0.31
	B2	J/g	20170	81	0.4	Robust mean	0.27
	K1	J/g	29342	59	0.2	Robust mean	0.20
S_d	B1	w%	0.20	0.01	4.2	Mean	0.28
	K1	w%	0.35	0.02	4.3	Robust mean	0.29
V_{db}	B1	w%	69.7	0.6	0.8	Mean	0.27
	B2	w%	85.0	0.3	0.4	Mean	0.13
	K1	w%	35.5	0.3	0.9	Mean	0.30

U_{pt} = Expanded uncertainty of the assigned value
Criterion for reliability of the assigned value $u_{pt}/s_{pt} \leq 0.3$, where
s_{pt}= target value of the standard deviation for proficiency assessment
u_{pt}= standard uncertainty of the assigned value

If $u_{pt}/s_{pt} \leq 0.3$, the assigned value is reliable and the z scores are qualified.

APPENDIX 6: Terms in the results tables

Results of each participant

Measurand	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - x_{pt})/s_{pt}$, where x_i = the result of the individual participant x_{pt} = the assigned value s_{pt} = the standard deviation for proficiency assessment
Assigned value	The value attributed to a particular property of a proficiency test item
2 × s_{pt} %	The standard deviation for proficiency assessment (s_{pt}) at the 95 % confidence level
Participants's result	The result reported by the participant (the mean value of the replicates)
Md	Median
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \leq z \leq 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than 2 × s_{pt} from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than 2 × s_{pt} from the assigned value
U – unsatisfactory ($z \geq 3$), positive error, the result deviates more than 3 × s_{pt} from the assigned value
u – unsatisfactory ($z \leq -3$), negative error, the result deviates more than 3 × s_{pt} from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i (i = 1, 2, ...,p)
s^* = 1.483 × median of $|x_i - x^*|$ (i = 1, 2, ...,p)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \times s^*$. A new value is then calculated for each result x_i $(i = 1, 2 \ldots p)$:

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134\sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 7: Results of each participant

Participant 1												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		-0.12	0.27	30	0.27	0.28	0.27	0.03	12.4	15
	w%	K1		0.25	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
C_d	w%	B2		0.17	50.8	2.5	50.9	50.9	50.8	0.7	1.4	11
	w%	K1		-0.16	71.9	2.5	71.8	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	K1		0.08	93.6	4	93.8	93.6	93.6	0.9	1.0	8
H_d	w%	B2		-0.01	6.04	6	6.04	6.04	6.04	0.04	0.7	9
	w%	K1		-0.56	4.69	6	4.61	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B2			8.26		8.56	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.33	4.39	4.41	0.16	3.7	18
N_d	w%	B2			0.076		0.072	0.072	0.076	0.020	27.1	8
	w%	K1		-0.06	2.21	10	2.20	2.22	2.21	0.07	3.2	9
$q_{p,net,d}$	J/g	B2		-0.11	18881	1.7	18864	18876	18881	32	0.2	9
	J/g	K1		-0.21	28343	1.1	28311	28330	28343	120	0.4	12
$q_{V,gr,d}$	J/g	B2		0.05	20170	1.5	20178	20224	20161	152	0.8	15
	J/g	K1		-0.29	29342	1	29299	29339	29343	89	0.3	17
S_d	w%	K1		-0.76	0.35	15	0.33	0.35	0.35	0.02	7.0	15

Participant 2												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		0.12	0.27	30	0.28	0.28	0.27	0.03	12.4	15
$M_{ad,d}$	w%	B2			8.26		8.24	8.30	8.24	0.33	4.1	19
$q_{p,net,d}$	J/g	B2		-0.03	18881	1.7	18876	18876	18881	32	0.2	9
$q_{V,gr,d}$	J/g	B2		0.35	20170	1.5	20224	20224	20161	152	0.8	15

Participant 3												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		1.05	3.14	8	3.27	3.16	3.14	0.15	4.8	11
	w%	B2		0.40	0.27	30	0.29	0.28	0.27	0.03	12.4	15
$M_{ad,d}$	w%	B1			6.17		6.36	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.51	8.30	8.24	0.33	4.1	19
$q_{p,net,d}$	J/g	B1		0.68	21189	1.5	21298	21147	21189	102	0.5	6
	J/g	B2		0.02	18881	1.7	18884	18876	18881	32	0.2	9
$q_{V,gr,d}$	J/g	B1		0.66	22408	1.3	22505	22400	22408	132	0.6	10
	J/g	B2		0.39	20170	1.5	20229	20224	20161	152	0.8	15

Participant 4												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-1.00	3.14	8	3.02	3.16	3.14	0.15	4.8	11
	w%	B2		-2.47	0.27	30	0.17	0.28	0.27	0.03	12.4	15
$M_{ad,d}$	w%	B1			6.17		5.28	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		7.37	8.30	8.24	0.33	4.1	19

Participant 5												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.16	3.14	8	3.16	3.16	3.14	0.15	4.8	11
	w%	B2		-3.70	0.27	30	0.12	0.28	0.27	0.03	12.4	15
	w%	K1		-0.36	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
$M_{ad,d}$	w%	B1			6.17		6.55	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.43	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		3.47	4.39	4.41	0.16	3.7	18
$q_{V,gr,d}$	J/g	B1		-1.84	22408	1.3	22140	22400	22408	132	0.6	10
	J/g	B2		0.36	20170	1.5	20225	20224	20161	152	0.8	15
	J/g	K1		-0.75	29342	1	29232	29339	29343	89	0.3	17
S_d	w%	B1		-0.10	0.20	15	0.20	0.20	0.20	0.01	5.6	7
	w%	K1		1.01	0.35	15	0.38	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		0.99	69.7	3	70.7	69.6	69.7	0.8	1.1	7
	w%	B2		0.30	85.0	3	85.4	85.1	85.0	0.4	0.5	6
	w%	K1		0.52	35.5	3	35.8	35.5	35.5	0.4	1.2	8

Participant 6												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		0.84	11.0	2.5	11.1	11.0	11.1	0.1	0.6	17
H_d	w%	K1		2.54	4.69	6	5.05	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	K1			4.36		4.32	4.39	4.41	0.16	3.7	18
$q_{V,gr,d}$	J/g	K1		-0.02	29342	1	29339	29339	29343	89	0.3	17
V_{db}	w%	K1		6.82	35.5	3	39.1	35.5	35.5	0.4	1.2	8

Participant 7												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
C_d	w%	B2		2.36	50.8	2.5	52.3	50.9	50.8	0.7	1.4	11
$M_{ad,d}$	w%	B2			8.26		8.08	8.30	8.24	0.33	4.1	19
$q_{V,gr,d}$	J/g	B2		-6.76	20170	1.5	19147	20224	20161	152	0.8	15

Participant 8												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		-1.60	11.0	2.5	10.8	11.0	11.1	0.1	0.6	17
C_d	w%	K1		11.58	71.9	2.5	82.3	71.8	72.0	0.9	1.3	14
$M_{ad,d}$	w%	K1			4.36		4.14	4.39	4.41	0.16	3.7	18
$q_{p,net,d}$	J/g	K1		-139.16	28343	1,1	6650	28330	28343	120	0.4	12
$q_{V,gr,d}$	J/g	K1		-156.02	29342	1	6453	29339	29343	89	0.3	17
S_d	w%	K1		-2.29	0.35	15	0.29	0.35	0.35	0.02	7.0	15
V_{db}	w%	K1		6.08	35.5	3	38.7	35.5	35.5	0.4	1.2	8

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-1.95	3.14	8	2.90	3.16	3.14	0.15	4.8	11
	w%	B2		-0.12	0.27	30	0.27	0.28	0.27	0.03	12.4	15
	w%	K1		1.27	11.0	2.5	11.2	11.0	11.1	0.1	0.6	17
$M_{ad,d}$	w%	B1			6.17		6.28	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		7.89	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.41	4.39	4.41	0.16	3.7	18

Participant 9												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{v,gr,d}$	J/g	B1		-0.39	22408	1.3	22352	22400	22408	132	0.6	10
	J/g	B2		-1.99	20170	1.5	19869	20224	20161	152	0.8	15
	J/g	K1		-0.15	29342	1	29320	29339	29343	89	0.3	17
S_d	w%	B1		0.17	0.20	15	0.20	0.20	0.20	0.01	5.6	7
	w%	K1		-0.51	0.35	15	0.34	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		-1.18	69.7	3	68.5	69.6	69.7	0.8	1.1	7
	w%	B2		-4.02	85.0	3	79.9	85.1	85.0	0.4	0.5	6
	w%	K1		-7.05	35.5	3	31.7	35.5	35.5	0.4	1.2	8

Participant 10												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		-0.25	0.27	30	0.26	0.28	0.27	0.03	12.4	15
	w%	K1		0.55	11.0	2.5	11.1	11.0	11.1	0.1	0.6	17
C_d	w%	B2		0.16	50.8	2.5	50.9	50.9	50.8	0.7	1.4	11
	w%	K1		-0.13	71.9	2.5	71.8	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	K1		0.21	93.6	4	94.0	93.6	93.6	0.9	1.0	8
H_d	w%	B2		-0.08	6.04	6	6.03	6.04	6.04	0.04	0.7	9
	w%	K1		0.00	4.69	6	4.69	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B2			8.26		8.86	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.38	4.39	4.41	0.16	3.7	18
N_d	w%	B2			0.076		0.075	0.072	0.076	0.020	27.1	8
	w%	K1		0.06	2.21	10	2.22	2.22	2.21	0.07	3.2	9
$q_{p,net,d}$	J/g	B2		0.30	18881	1.7	18929	18876	18881	32	0.2	9
	J/g	K1		-0.73	28343	1.1	28229	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	B2		0.47	20170	1.5	20241	20224	20161	152	0.8	15
	J/g	K1		-0.75	29342	1	29233	29339	29343	89	0.3	17
S_d	w%	K1		-0.80	0.35	15	0.33	0.35	0.35	0.02	7.0	15
V_{db}	w%	B2		0.13	85.0	3	85.2	85.1	85.0	0.4	0.5	6
	w%	K1		-0.30	35.5	3	35.3	35.5	35.5	0.4	1.2	8

Participant 11												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		1.16	11.0	2.5	11.2	11.0	11.1	0.1	0.6	17
C_d	w%	K1		-0.26	71.9	2.5	71.7	71.8	72.0	0.9	1.3	14
$M_{ad,d}$	w%	K1			4.36		4.51	4.39	4.41	0.16	3.7	18
$q_{p,net,d}$	J/g	K1		-0.28	28343	1.1	28300	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	K1		-0.18	29342	1	29315	29339	29343	89	0.3	17
S_d	w%	K1		0.63	0.35	15	0.37	0.35	0.35	0.02	7.0	15
V_{db}	w%	K1		-1.25	35.5	3	34.8	35.5	35.5	0.4	1.2	8

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
C_d	w%	B2		-2.12	50.8	2.5	49.5	50.9	50.8	0.7	1.4	11
	w%	K1		1.79	71.9	2.5	73.5	71.8	72.0	0.9	1.3	14
H_d	w%	B2		-0.39	6.04	6	5.97	6.04	6.04	0.04	0.7	9
	w%	K1		1.11	4.69	6	4.85	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B2			8.26		8.30	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.81	4.39	4.41	0.16	3.7	18

Participant 12												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
N_d	w%	B2			0.076		0.196	0.072	0.076	0.020	27.1	8
	w%	K1		1.03	2.21	10	2.32	2.22	2.21	0.07	3.2	9
$q_{p,net,d}$	J/g	B2		-8.83	18881	1.7	17465	18876	18881	32	0.2	9
	J/g	K1		0.98	28343	1.1	28496	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	B2		-7.86	20170	1.5	18981	20224	20161	152	0.8	15
	J/g	K1		1.03	29342	1	29494	29339	29343	89	0.3	17
S_d	w%	K1		-0.67	0.35	15	0.33	0.35	0.35	0.02	7.0	15
V_{db}	w%	B2		1.56	85.0	3	87.0	85.1	85.0	0.4	0.5	6
	w%	K1		1.15	35.5	3	36.1	35.5	35.5	0.4	1.2	8

Participant 13												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		-1.11	0.27	30	0.23	0.28	0.27	0.03	12.4	15
	w%	K1		-1.45	11.0	2.5	10.8	11.0	11.1	0.1	0.6	17
C_d	w%	B2		1.11	50.8	2.5	51.5	50.9	50.8	0.7	1.4	11
	w%	K1		0.27	71.9	2.5	72.1	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	K1		1.00	93.6	4	95.5	93.6	93.6	0.9	1.0	8
H_d	w%	B2		0.30	6.04	6	6.10	6.04	6.04	0.04	0.7	9
	w%	K1		-2.24	4.69	6	4.38	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B2			8.26		7.91	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.18	4.39	4.41	0.16	3.7	18
$q_{p,net,d}$	J/g	B2		-1.29	18881	1.7	18674	18876	18881	32	0.2	9
	J/g	K1		1.41	28343	1.1	28564	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	B2		-1.11	20170	1.5	20002	20224	20161	152	0.8	15
	J/g	K1		1.09	29342	1	29502	29339	29343	89	0.3	17
S_d	w%	K1		2.29	0.35	15	0.41	0.35	0.35	0.02	7.0	15

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.52	3.14	8	3.21	3.16	3.14	0.15	4.8	11
	w%	B2		0.12	0.27	30	0.28	0.28	0.27	0.03	12.4	15
	w%	K1		0.29	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
C_d	w%	B1			55.4		55.1	55.3	55.4	0.4	0.7	5
	w%	B2		-0.30	50.8	2.5	50.6	50.9	50.8	0.7	1.4	11
	w%	K1		-0.28	71.9	2.5	71.7	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	B1			102		102	102	102	1	0.5	4
	t CO2/TJ	K1		-0.08	93.6	4	93.5	93.6	93.6	0.9	1.0	8
H_d	w%	B1					7.36	5.87	5.95	0.19	3.1	4
	w%	B2		1.08	6.04	6	6.24	6.04	6.04	0.04	0.7	9
	w%	K1		1.34	4.69	6	4.88	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B1			6.17		5.83	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.09	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.39	4.39	4.41	0.16	3.7	18
N_d	w%	B1			1.75		1.76	1.76	1.75	0.08	4.5	5
	w%	B2			0.076		0.110	0.072	0.076	0.020	27.1	8
	w%	K1		0.32	2.21	10	2.25	2.22	2.21	0.07	3.2	9

Participant 14												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{p,net,d}$	J/g	B1		-0.36	21189	1.5	21132	21147	21189	102	0.5	6
	J/g	B2		0.03	18881	1.7	18886	18876	18881	32	0.2	9
	J/g	K1		0.00	28343	1.1	28343	28330	28343	120	0.4	12
$q_{V,gr,d}$	J/g	B1		0.03	22408	1.3	22413	22400	22408	132	0.6	10
	J/g	B2		0.43	20170	1.5	20236	20224	20161	152	0.8	15
	J/g	K1		0.35	29342	1	29393	29339	29343	89	0.3	17
S_d	w%	B1		-0.23	0.20	15	0.20	0.20	0.20	0.01	5.6	7
	w%	K1		0.30	0.35	15	0.36	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		0.47	69.7	3	70.2	69.6	69.7	0.8	1.1	7
	w%	B2		0.17	85.0	3	85.2	85.1	85.0	0.4	0.5	6
	w%	K1		0.52	35.5	3	35.8	35.5	35.5	0.4	1.2	8

Participant 15												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-0.92	3.14	8	3.03	3.16	3.14	0.15	4.8	11
	w%	B2		0.12	0.27	30	0.28	0.28	0.27	0.03	12.4	15
	w%	K1		-0.15	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
C_d	w%	B1			55.4		55.3	55.3	55.4	0.4	0.7	5
	w%	B2		-0.30	50.8	2.5	50.6	50.9	50.8	0.7	1.4	11
	w%	K1		-0.21	71.9	2.5	71.7	71.8	72.0	0.9	1.3	14
H_d	w%	B1					5.90	5.87	5.95	0.19	3.1	4
	w%	B2		-0.14	6.04	6	6.02	6.04	6.04	0.04	0.7	9
	w%	K1		-0.21	4.69	6	4.66	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B1			6.17		6.25	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.36	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.48	4.39	4.41	0.16	3.7	18
N_d	w%	B1			1.75		1.72	1.76	1.75	0.08	4.5	5
	w%	B2			0.076		0.100	0.072	0.076	0.020	27.1	8
	w%	K1		-0.72	2.21	10	2.13	2.22	2.21	0.07	3.2	9
$q_{V,gr,d}$	J/g	B1		1.11	22408	1.3	22570	22400	22408	132	0.6	10
	J/g	B2		1.79	20170	1.5	20441	20224	20161	152	0.8	15
	J/g	K1		0.56	29342	1	29425	29339	29343	89	0.3	17
S_d	w%	K1		0.76	0.35	15	0.37	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		-0.34	69.7	3	69.3	69.6	69.7	0.8	1.1	7
	w%	B2		-0.13	85.0	3	84.8	85.1	85.0	0.4	0.5	6
	w%	K1		-0.52	35.5	3	35.2	35.5	35.5	0.4	1.2	8

Participant 16												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
C_d	w%	B2		-2.48	50.8	2.5	49.2	50.9	50.8	0.7	1.4	11
H_d	w%	B2		0.31	6.04	6	6.10	6.04	6.04	0.04	0.7	9
$M_{ad,d}$	w%	B2			8.26		8.13	8.30	8.24	0.33	4.1	19
N_d	w%	B2			0.076		0.412	0.072	0.076	0.020	27.1	8

Participant 17												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-1.55	3.14	8	2.95	3.16	3.14	0.15	4.8	11
	w%	B2		-1.23	0.27	30	0.22	0.28	0.27	0.03	12.4	15
	w%	K1		-0.15	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
$M_{ad,d}$	w%	B1			6.17		6.81	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.48	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.41	4.39	4.41	0.16	3.7	18
$q_{v,gr,d}$	J/g	B1		-0.73	22408	1.3	22302	22400	22408	132	0.6	10
	J/g	B2		-1.99	20170	1.5	19870	20224	20161	152	0.8	15
	J/g	K1		-0.50	29342	1	29269	29339	29343	89	0.3	17
S_d	w%	B1		-1.67	0.20	15	0.18	0.20	0.20	0.01	5.6	7
	w%	K1		-0.57	0.35	15	0.34	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		-0.32	69.7	3	69.4	69.6	69.7	0.8	1.1	7
	w%	K1		-4.49	35.5	3	33.1	35.5	35.5	0.4	1.2	8

Participant 18												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		1.39	3.14	8	3.32	3.16	3.14	0.15	4.8	11
	w%	B2		1.14	0.27	30	0.32	0.28	0.27	0.03	12.4	15
	w%	K1		0.62	11.0	2.5	11.1	11.0	11.1	0.1	0.6	17
C_d	w%	B1			55.4		54.9	55.3	55.4	0.4	0.7	5
	w%	B2		-0.88	50.8	2.5	50.2	50.9	50.8	0.7	1.4	11
	w%	K1		-1.17	71.9	2.5	70.8	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	B1			102		101	102	102	1	0.5	4
	t CO2/TJ	K1		-0.76	93.6	4	92.2	93.6	93.6	0.9	1.0	8
H_d	w%	B1					6.23	5.87	5.95	0.19	3.1	4
	w%	B2		2.01	6.04	6	6.41	6.04	6.04	0.04	0.7	9
	w%	K1		-1.33	4.69	6	4.50	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B1			6.17		5.85	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.22	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.68	4.39	4.41	0.16	3.7	18
N_d	w%	B1			1.75		1.63	1.76	1.75	0.08	4.5	5
	w%	B2			0.076		0.049	0.072	0.076	0.020	27.1	8
	w%	K1		-1.17	2.21	10	2.08	2.22	2.21	0.07	3.2	9
$q_{p,net,d}$	J/g	B1		-0.64	21189	1.5	21088	21147	21189	102	0.5	6
	J/g	B2		-0.17	18881	1.7	18853	18876	18881	32	0.2	9
	J/g	K1		0.49	28343	1.1	28420	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	B1		0.20	22408	1.3	22438	22400	22408	132	0.6	10
	J/g	B2		0.51	20170	1.5	20247	20224	20161	152	0.8	15
	J/g	K1		0.30	29342	1	29386	29339	29343	89	0.3	17
S_d	w%	B1		0.63	0.20	15	0.21	0.20	0.20	0.01	5.6	7
	w%	K1		0.69	0.35	15	0.37	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		0.51	69.7	3	70.2	69.6	69.7	0.8	1.1	7
	w%	B2		0.08	85.0	3	85.1	85.1	85.0	0.4	0.5	6
	w%	K1		0.28	35.5	3	35.7	35.5	35.5	0.4	1.2	8

Participant 19												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		0.22	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
C_d	w%	K1		0.00	71.9	2.5	71.9	71.8	72.0	0.9	1.3	14
H_d	w%	K1		-0.29	4.69	6	4.65	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	K1			4.36		4.29	4.39	4.41	0.16	3.7	18
$q_{p,net,d}$	J/g	K1		0.25	28343	1.1	28382	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	K1		0.39	29342	1	29400	29339	29343	89	0.3	17
S_d	w%	K1		0.02	0.35	15	0.35	0.35	0.35	0.02	7.0	15

Participant 20												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		1.35	3.14	8	3.31	3.16	3.14	0.15	4.8	11
	w%	B2		1.48	0.27	30	0.33	0.28	0.27	0.03	12.4	15
$M_{ad,d}$	w%	B1			6.17		6.01	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		7.91	8.30	8.24	0.33	4.1	19
$q_{p,net,d}$	J/g	B1		-0.17	21189	1.5	21162	21147	21189	102	0.5	6
	J/g	B2		-0.30	18881	1.7	18834	18876	18881	32	0.2	9
$q_{v,gr,d}$	J/g	B1		-0.17	22408	1.3	22384	22400	22408	132	0.6	10
	J/g	B2		-0.14	20170	1.5	20149	20224	20161	152	0.8	15

Participant 21												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		0.55	11.0	2.5	11.1	11.0	11.1	0.1	0.6	17
C_d	w%	K1		1.01	71.9	2.5	72.8	71.8	72.0	0.9	1.3	14
$M_{ad,d}$	w%	K1			4.36		3.89	4.39	4.41	0.16	3.7	18
$q_{p,net,d}$	J/g	K1		-1.37	28343	1.1	28129	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	K1		-0.70	29342	1	29240	29339	29343	89	0.3	17

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		0.92	3.14	8	3.26	3.16	3.14	0.15	4.8	11
	w%	B2		0.62	0.27	30	0.30	0.28	0.27	0.03	12.4	15
	w%	K1		0.25	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
C_d	w%	B1			55.4		55.8	55.3	55.4	0.4	0.7	5
	w%	B2		0.11	50.8	2.5	50.9	50.9	50.8	0.7	1.4	11
	w%	K1		-0.38	71.9	2.5	71.6	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	B1			102		102	102	102	1	0.5	4
	t CO2/TJ	K1		-0.08	93.6	4	93.5	93.6	93.6	0.9	1.0	8
H_d	w%	B1					5.84	5.87	5.95	0.19	3.1	4
	w%	B2		-0.23	6.04	6	6.00	6.04	6.04	0.04	0.7	9
	w%	K1		1.11	4.69	6	4.85	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B1			6.17		6.60	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.64	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.23	4.39	4.41	0.16	3.7	18
N_d	w%	B1			1.75		1.82	1.76	1.75	0.08	4.5	5
	w%	B2			0.076		0.071	0.072	0.076	0.020	27.1	8
	w%	K1		0.35	2.21	10	2.25	2.22	2.21	0.07	3.2	9

Participant 22												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{p,net,d}$	J/g	B1		0.91	21189	1.5	21334	21147	21189	102	0.5	6
	J/g	B2		-0.04	18881	1.7	18875	18876	18881	32	0.2	9
	J/g	K1		-0.17	28343	1.1	28317	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	B1		1.25	22408	1.3	22590	22400	22408	132	0.6	10
	J/g	B2		0.12	20170	1.5	20188	20224	20161	152	0.8	15
	J/g	K1		0.09	29342	1	29355	29339	29343	89	0.3	17
S_d	w%	B1		-0.47	0.20	15	0.19	0.20	0.20	0.01	5.6	7
	w%	K1		-1.12	0.35	15	0.32	0.35	0.35	0.02	7.0	15
V_{db}	w%	B1		-0.12	69.7	3	69.6	69.6	69.7	0.8	1.1	7
	w%	B2		-0.56	85.0	3	84.3	85.1	85.0	0.4	0.5	6
	w%	K1		-0.81	35.5	3	35.1	35.5	35.5	0.4	1.2	8

Participant 23												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B2		-1.36	0.27	30	0.22	0.28	0.27	0.03	12.4	15
	w%	K1		-0.18	11.0	2.5	11.0	11.0	11.1	0.1	0.6	17
C_d	w%	B2		-0.46	50.8	2.5	50.5	50.9	50.8	0.7	1.4	11
	w%	K1		-1.05	71.9	2.5	71.0	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	K1		-0.36	93.6	4	92.9	93.6	93.6	0.9	1.0	8
H_d	w%	B2		-0.01	6.04	6	6.04	6.04	6.04	0.04	0.7	9
	w%	K1		-0.56	4.69	6	4.61	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B2			8.26		8.36	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.39	4.39	4.41	0.16	3.7	18
N_d	w%	B2			0.076		0.072	0.072	0.076	0.020	27.1	8
	w%	K1		-0.05	2.21	10	2.20	2.22	2.21	0.07	3.2	9
$q_{p,net,d}$	J/g	B2		-2.40	18881	1.7	18497	18876	18881	32	0.2	9
	J/g	K1		-0.74	28343	1.1	28227	28330	28343	120	0.4	12
$q_{v,gr,d}$	J/g	B2		-2.37	20170	1.5	19811	20224	20161	152	0.8	15
	J/g	K1		-0.87	29342	1	29214	29339	29343	89	0.3	17
S_d	w%	K1		-0.95	0.35	15	0.33	0.35	0.35	0.02	7.0	15
V_{db}	w%	K1		-4.36	35.5	3	33.2	35.5	35.5	0.4	1.2	8

Participant 24												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
$q_{v,gr,d}$	J/g	B2		-0.68	20170	1.5	20068	20224	20161	152	0.8	15

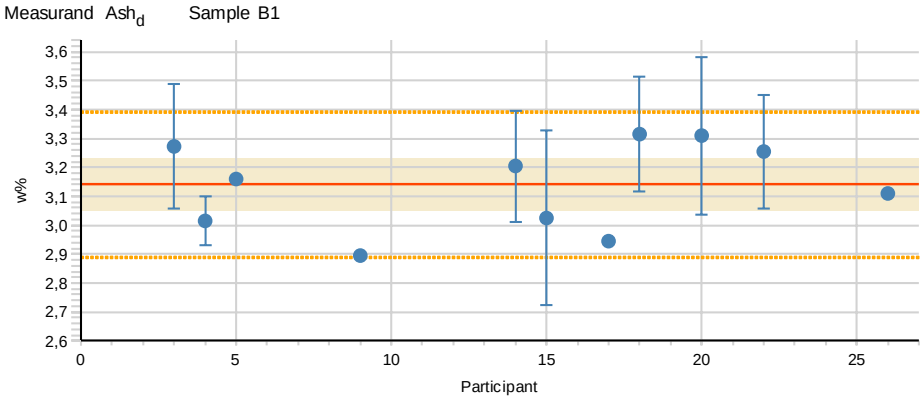
Participant 25												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	K1		-3.64	11.0	2.5	10.5	11.0	11.1	0.1	0.6	17
C_d	w%	K1		2.51	71.9	2.5	74.2	71.8	72.0	0.9	1.3	14
H_d	w%	K1		-1.07	4.69	6	4.54	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	K1			4.36		4.22	4.39	4.41	0.16	3.7	18
N_d	w%	K1		0.05	2.21	10	2.22	2.22	2.21	0.07	3.2	9

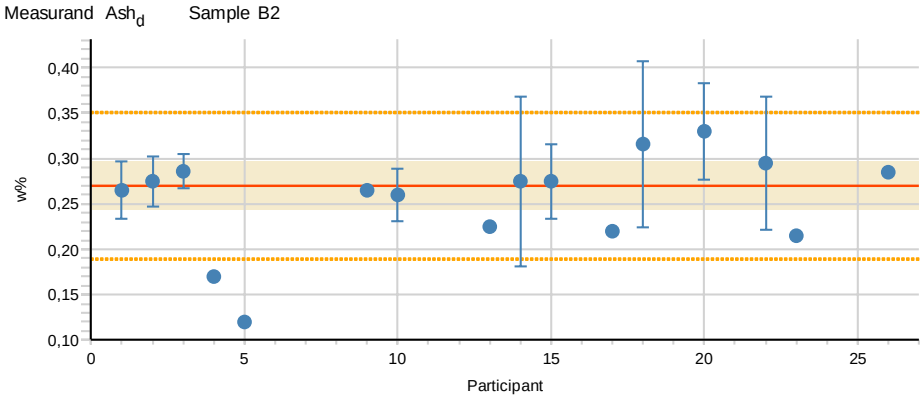
Participant 26												
Measurand	Unit	Sample	-3 0 3	z score	Assigned value	2×s_{pt} %	Participant's result	Md	Mean	SD	SD%	n (stat)
Ash_d	w%	B1		-0.24	3.14	8	3.11	3.16	3.14	0.15	4.8	11
	w%	B2		0.37	0.27	30	0.29	0.28	0.27	0.03	12.4	15
	w%	K1		0.80	11.0	2.5	11.1	11.0	11.1	0.1	0.6	17
C_d	w%	B1			55.4		55.7	55.3	55.4	0.4	0.7	5
	w%	B2		0.21	50.8	2.5	50.9	50.9	50.8	0.7	1.4	11
	w%	K1		0.23	71.9	2.5	72.1	71.8	72.0	0.9	1.3	14
EF	t CO2/TJ	B1			102		103	102	102	1	0.5	4
	t CO2/TJ	K1		0.16	93.6	4	93.9	93.6	93.6	0.9	1.0	8
H_d	w%	B1					5.85	5.87	5.95	0.19	3.1	4
	w%	B2		0.00	6.04	6	6.04	6.04	6.04	0.04	0.7	9
	w%	K1		0.25	4.69	6	4.73	4.66	4.69	0.13	2.7	11
$M_{ad,d}$	w%	B1			6.17		6.02	6.25	6.17	0.43	7.0	11
	w%	B2			8.26		8.30	8.30	8.24	0.33	4.1	19
	w%	K1			4.36		4.50	4.39	4.41	0.16	3.7	18
N_d	w%	B1			1.75		1.82	1.76	1.75	0.08	4.5	5
	w%	B2			0.076		0.057	0.072	0.076	0.020	27.1	8
	w%	K1		-2.55	2.21	10	1.93	2.22	2.21	0.07	3.2	9
$q_{p,net,d}$	J/g	B1		-0.43	21189	1.5	21121	21147	21189	102	0.5	6
	J/g	B2		0.30	18881	1.7	18930	18876	18881	32	0.2	9
	J/g	K1		0.38	28343	1.1	28403	28330	28343	120	0.4	12
$q_{V,gr,d}$	J/g	B1		-0.14	22408	1.3	22388	22400	22408	132	0.6	10
	J/g	B2		0.50	20170	1.5	20246	20224	20161	152	0.8	15
	J/g	K1		0.48	29342	1	29413	29339	29343	89	0.3	17
S_d	w%	B1		-0.63	0.20	15	0.19	0.20	0.20	0.01	5.6	7
	w%	K1		0.06	0.35	15	0.35	0.35	0.35	0.02	7.0	15

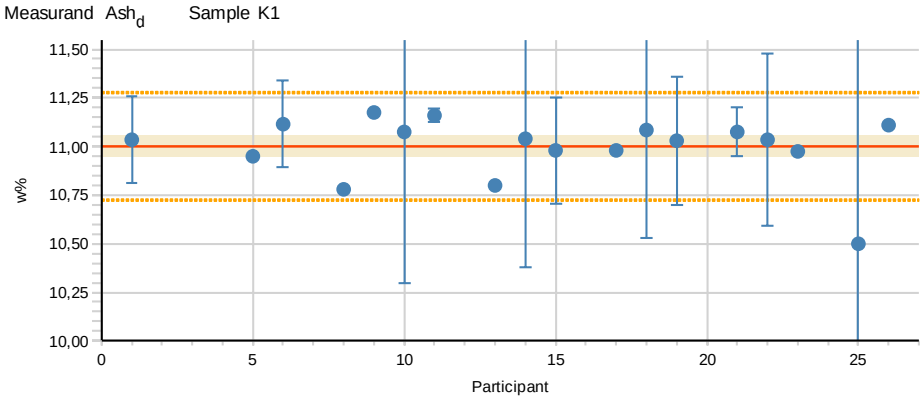
APPENDIX 8: Results of participants and their uncertainties

In figures:

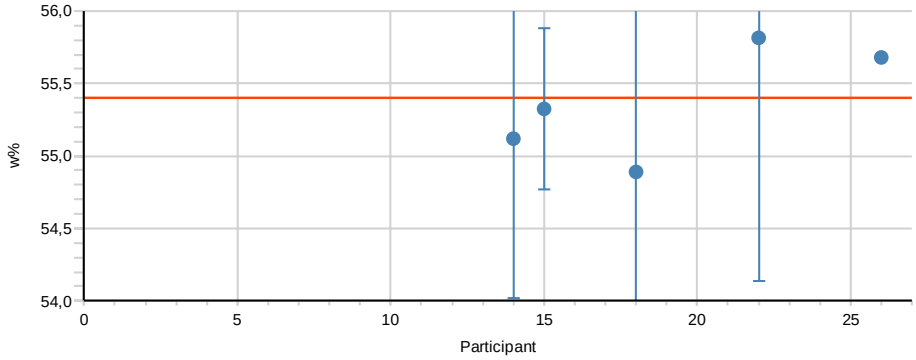
- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.



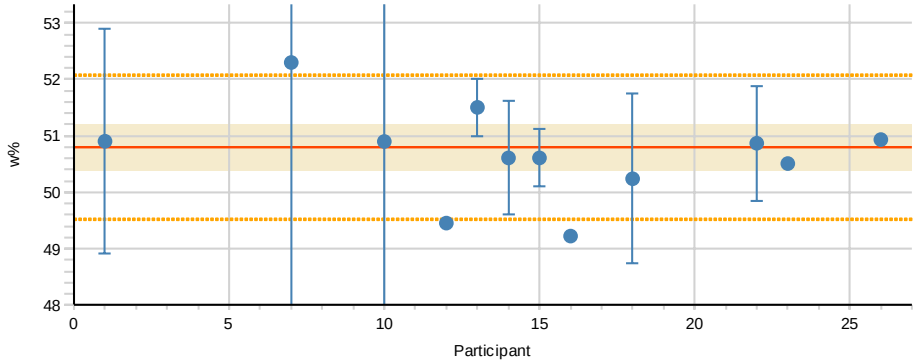




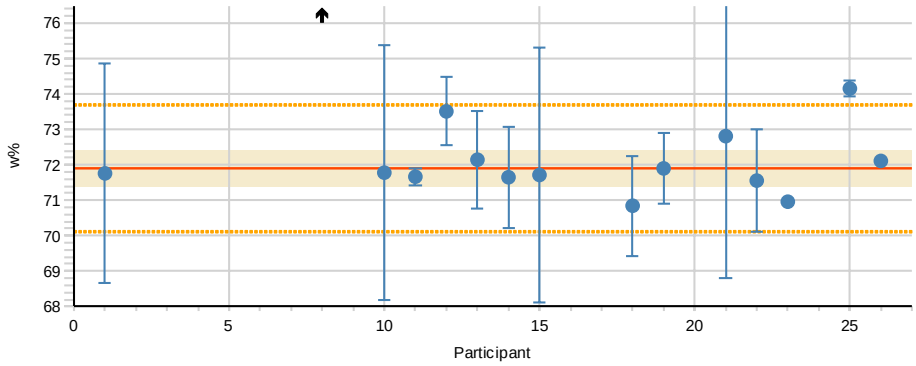
Measurand C_d Sample B1



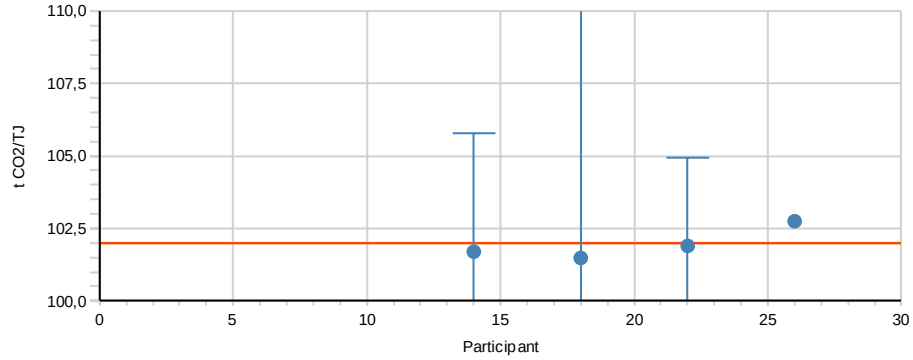
Measurand C_d Sample B2



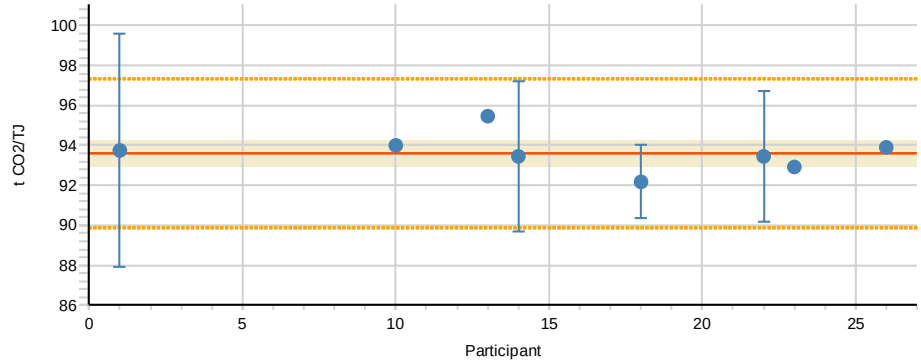
Measurand C_d Sample K1



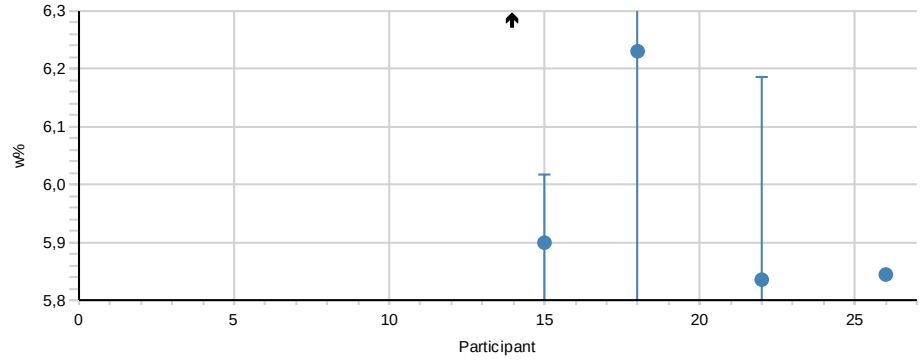
Measurand EF Sample B1

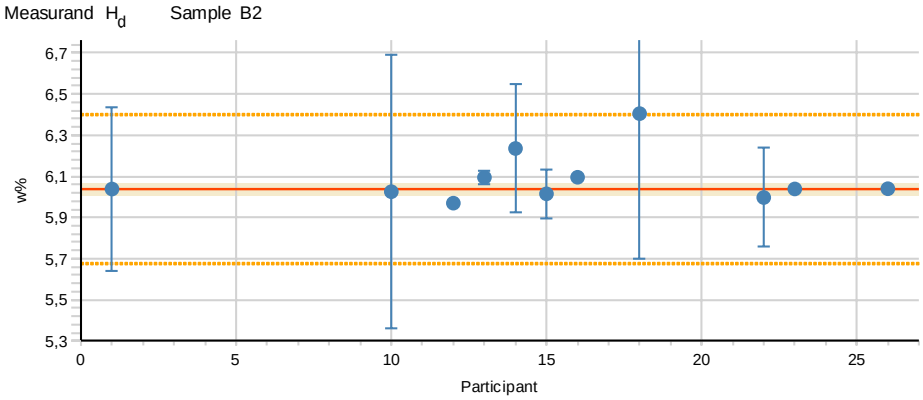


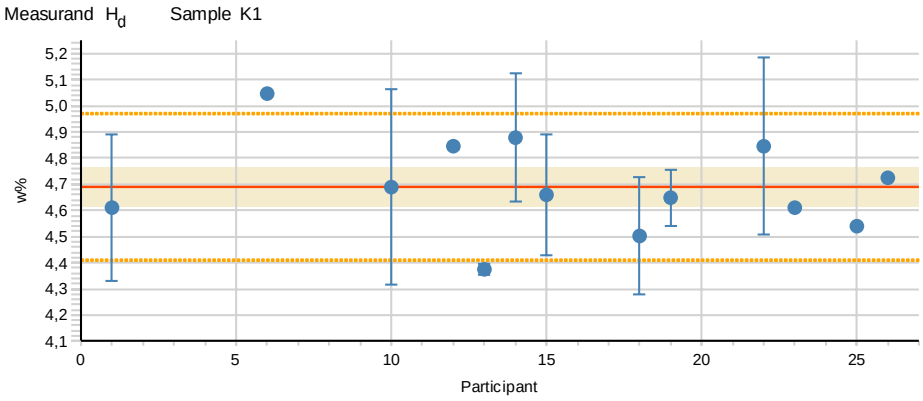
Measurand EF Sample K1

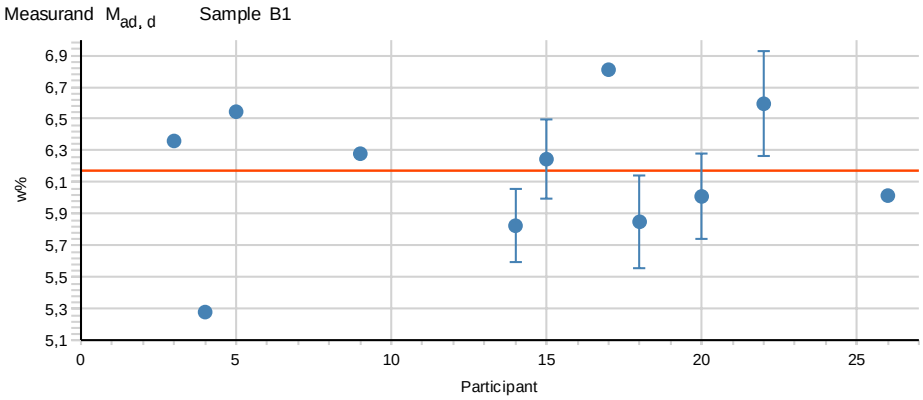


Measurand H_d Sample B1

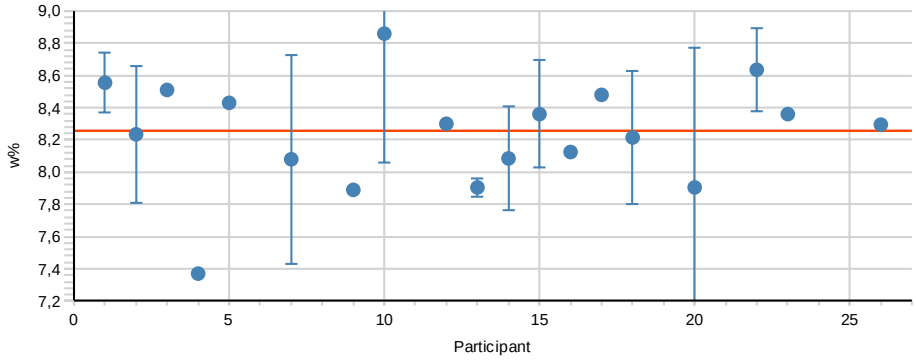



Measurand H_d Sample B2
w%
6,7
6,5
6,3
6,1
5,9
5,7
5,5
5,3
0
5
10
15
20
25
Participant

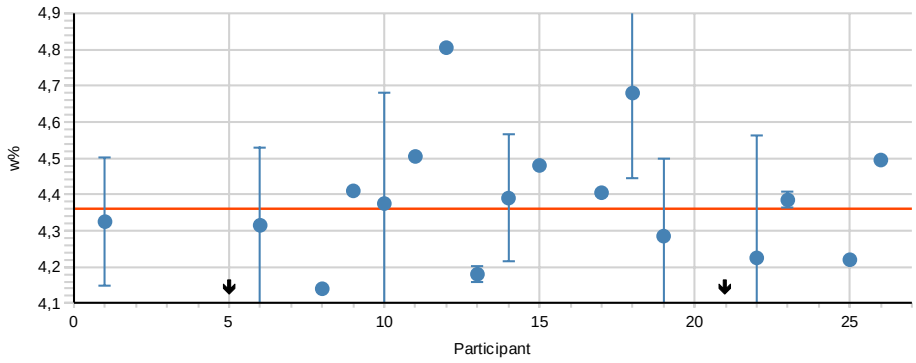

Measurand H_d Sample K1
w%
5,2
5,1
5,0
4,9
4,8
4,7
4,6
4,5
4,4
4,3
4,2
4,1
0
5
10
15
20
25
Participant


Measurand $M_{ad,\,d}$ Sample B1
w%
6,9
6,7
6,5
6,3
6,1
5,9
5,7
5,5
5,3
5,1
0
5
10
15
20
25
Participant

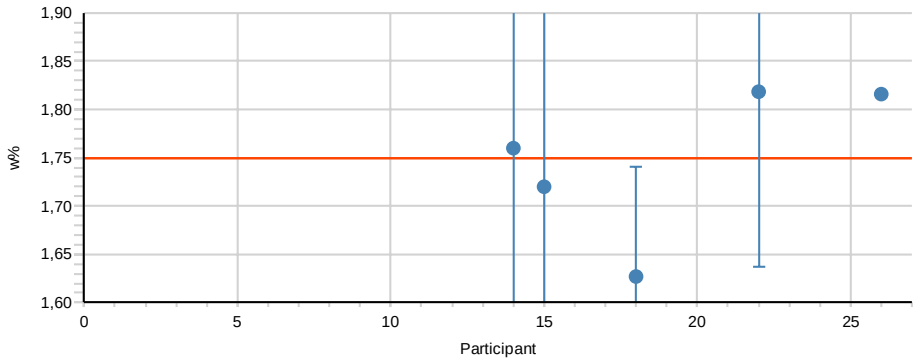
Measurand $M_{ad,\,d}$ Sample B2



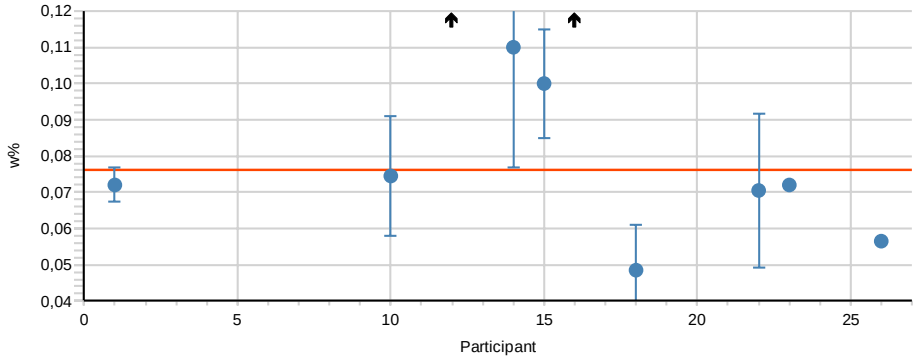
Measurand $M_{ad,\,d}$ Sample K1



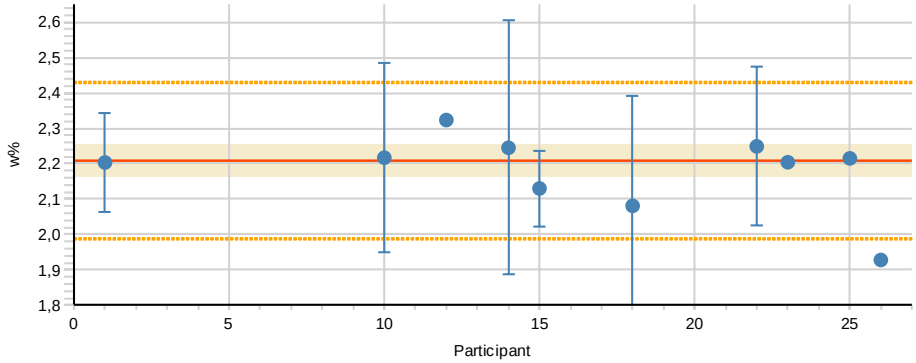
Measurand N_d Sample B1



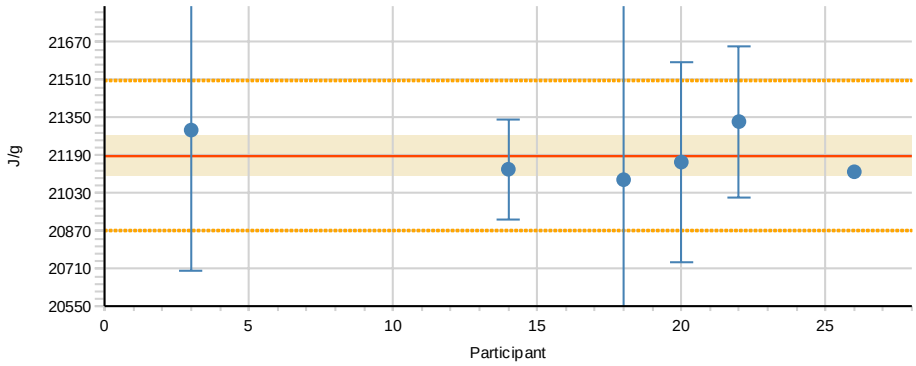
Measurand N_d Sample B2



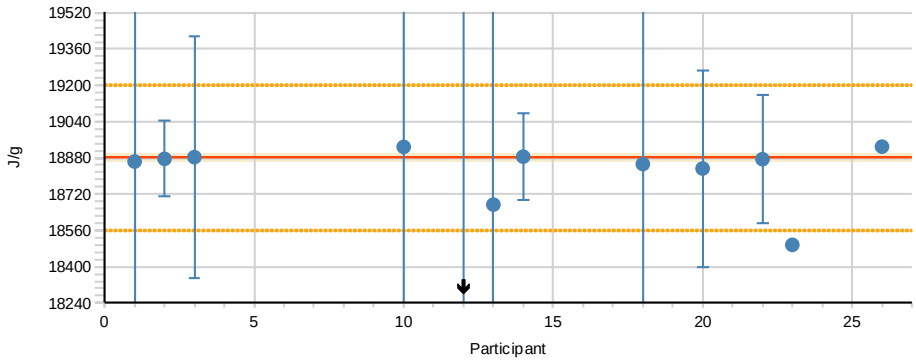
Measurand N_d Sample K1



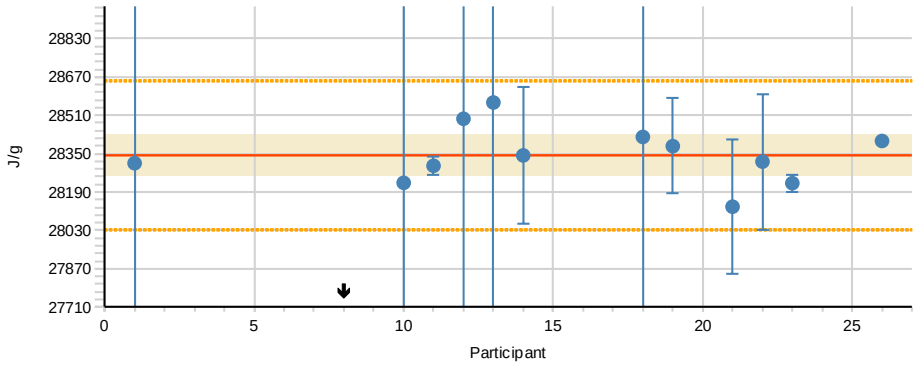
Measurand $q_{p,\,net,d}$ Sample B1



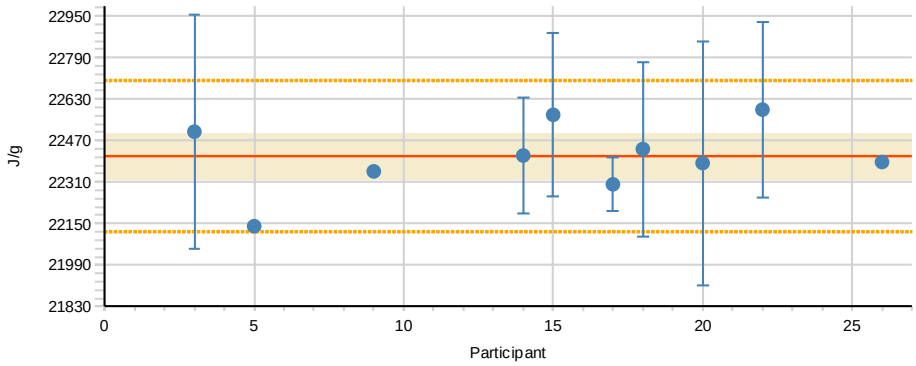
Measurand $q_{p,\,net,d}$ Sample B2

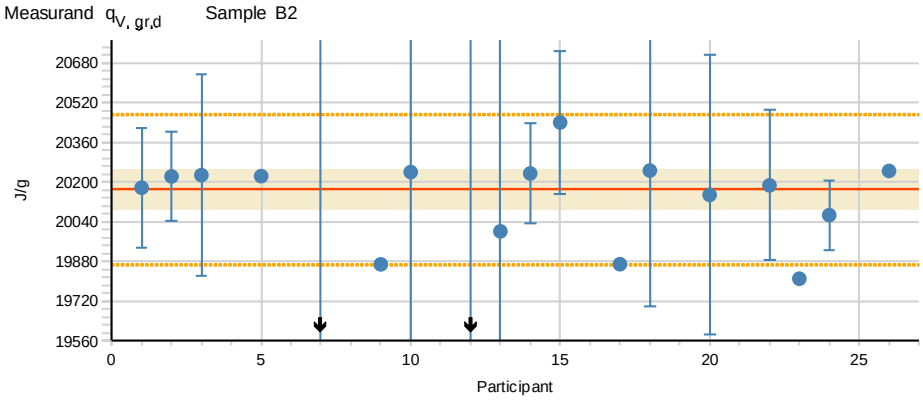


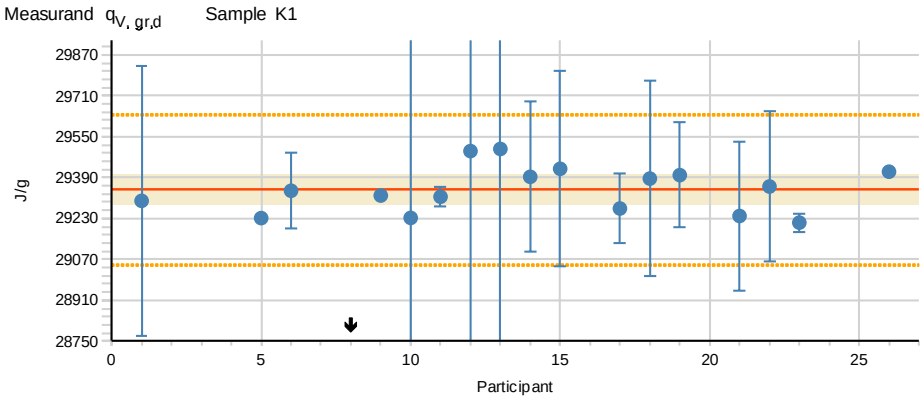
Measurand $q_{p,\,net,d}$ Sample K1

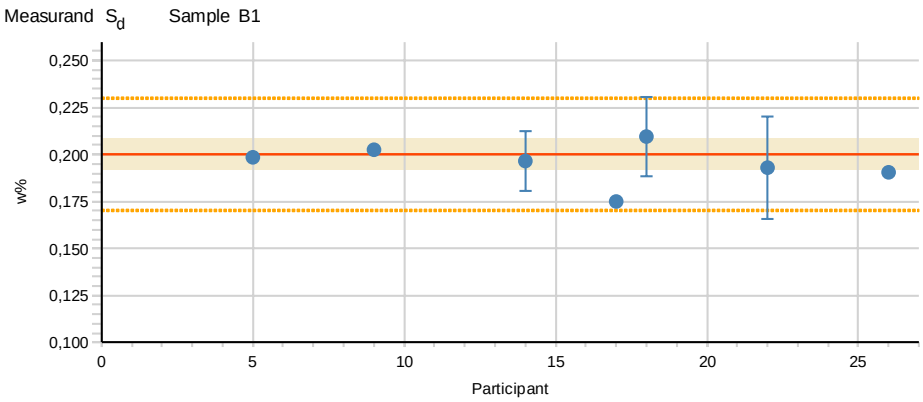


Measurand $q_{V,\,gr,d}$ Sample B1

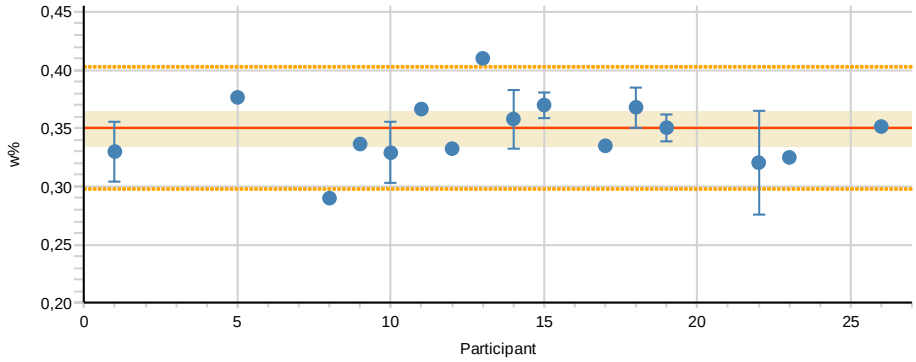



Measurand $q_{V, gr,d}$ Sample B2
J/g
20680
20520
20360
20200
20040
19880
19720
19560
0
5
10
15
20
25
Participant

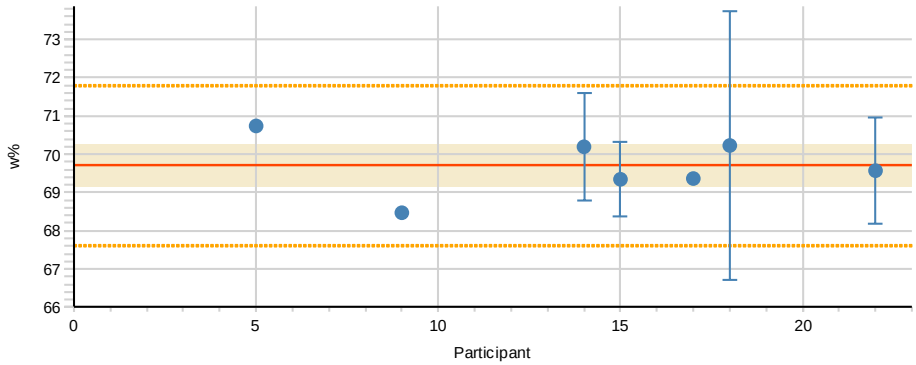

Measurand $q_{V, gr,d}$ Sample K1
J/g
29870
29710
29550
29390
29230
29070
28910
28750
0
5
10
15
20
25
Participant


Measurand S_d Sample B1
w%
0,250
0,225
0,200
0,175
0,150
0,125
0,100
0
5
10
15
20
25
Participant

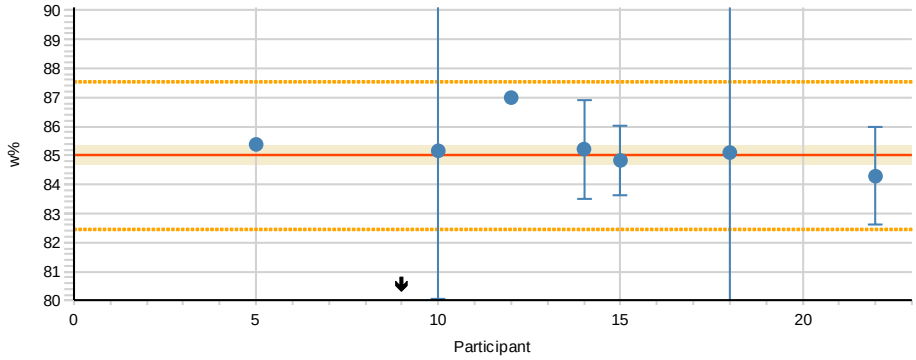
Measurand S_d Sample K1

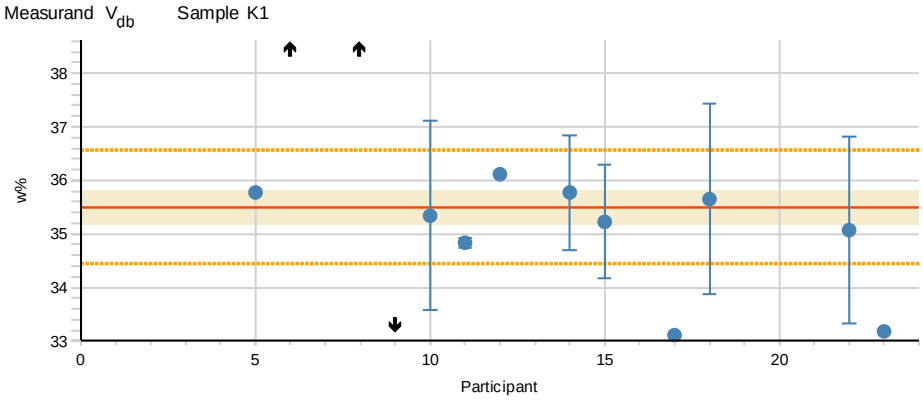


Measurand V_{db} Sample B1



Measurand V_{db} Sample B2




Measurand V_{db}
Sample K1
w%
38
37
36
35
34
33
0
5
10
15
20
Participant

APPENDIX 9: Summary of the z and E_n scores

Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
Ash_d	B1	.	.	S	S	S	.	.	.	S	.	.	.	.	S	S	.	S	S	.	S	.	S	.	100
	B2	S	S	S	q	*u*	.	.	.	S	S	.	.	S	S	S	.	S	S	.	S	.	S	S	87.5
	K1	S	.	.	.	S	S	.	S	S	S	S	.	S	S	S	.	S	S	S	.	S	S	S	94.4
C_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	S	.	.	.	.	.	Q	.	.	S	.	*q*	S	S	S	*q*	.	S	.	.	.	S	S	75.0
	K1	S	.	.	.	.	.	.	U	.	S	S	S	S	S	S	.	.	S	S	.	S	S	S	86.7
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	*S*	.	.	.	.	.	.	.	.	*S*	.	.	*S*	S	.	.	.	S	.	.	.	S	S	100
H_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	S	.	.	.	.	.	.	.	.	S	.	*S*	S	S	S	*S*	.	Q	.	.	.	S	S	90.9
	K1	S	.	.	.	.	Q	.	.	.	S	.	S	q	S	S	.	.	S	S	.	.	S	S	84.6
N_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	S	.	.	.	.	.	.	.	.	S	.	S	.	S	S	.	.	S	.	.	.	S	S	90.0
$q_{p,net,d}$	B1	.	.	S	.	.	.	.	.	.	.	.	.	.	S	.	.	.	S	.	S	.	S	.	100
	B2	S	S	S	.	.	.	.	.	.	S	.	*u*	S	S	.	.	.	S	.	*S*	.	S	*q*	83.3
	K1	S	.	.	.	.	.	.	u	.	S	*S*	S	S	S	.	.	.	S	S	.	S	S	S	92.3
$q_{V,gr,d}$	B1	.	.	S	.	*S*	.	.	.	*S*	.	.	.	.	S	S	.	S	S	.	*S*	.	S	.	100
	B2	S	S	S	.	S	.	*u*	.	S	S	.	*u*	S	S	S	.	*S*	S	.	S	.	S	*q*	83.3
	K1	S	.	.	.	*S*	S	.	u	S	S	*S*	S	S	S	S	.	S	S	S	.	S	S	S	94.4
S_d	B1	.	.	.	.	*S*	.	.	.	*S*	.	.	.	.	S	.	.	*S*	S	.	.	.	S	.	100
	K1	S	.	.	.	S	.	.	*q*	S	S	*S*	S	Q	S	S	.	S	S	S	.	.	S	S	87.5
V_{db}	B1	.	.	.	.	*S*	.	.	.	*S*	.	.	.	.	S	S	.	S	S	.	.	.	*S*	.	100
	B2	.	.	.	.	S	.	.	.	*u*	S	.	*S*	.	S	S	.	.	S	.	.	.	S	.	87.5
	K1	.	.	.	.	*S*	U	.	U	*u*	S	*S*	*S*	.	S	S	.	*u*	S	.	.	.	*S*	*u*	61.5
%		100	100	100	50	91	50	0	17	82	100	100	75	83	100	100	50	90	95	100	100	100	100	79	
accredited		12	3	6	2		4	1	5		14		5	9	20	15		2	20	5		4	17	3	

Measurand	Sample	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	%
Ash_d	B1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87.5
	K1	.	*u*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	94.4
C_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	75.0
	K1	.	*Q*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	86.7
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	*S*	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
H_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.9
	K1	.	*S*	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	84.6
$M_{ad,d}$	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
N_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	
	K1	.	*S*	q	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	90.0
$q_{p,net,d}$	B1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	83.3
	K1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	92.3
$q_{V,gr,d}$	B1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	S	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	83.3
	K1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	94.4
S_d	B1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	K1	.	.	S	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87.5
V_{db}	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	100
	B2	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	87.5
	K1	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	61.5
%		100	50	94																					
accredited		1		16																					

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, italics - non-accredited, normal - other
% - percentage of satisfactory results

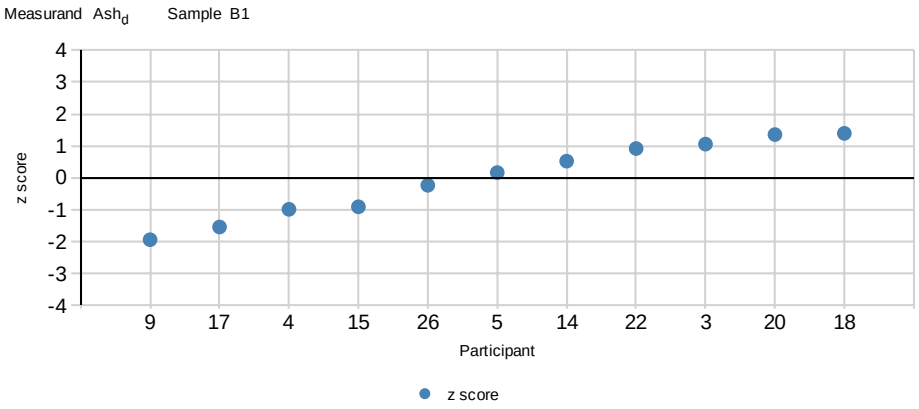
Totally satisfactory, % in all: 89 % in accredited: 93 % in non-accredited: 81

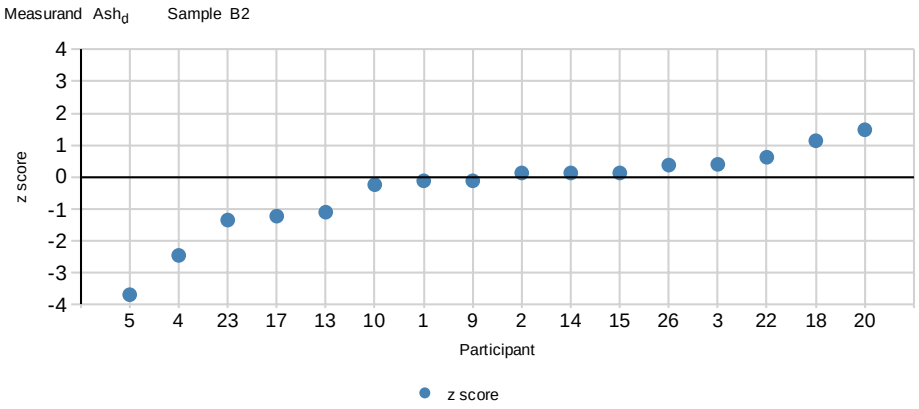
Summary of results evaluated based on E_n score

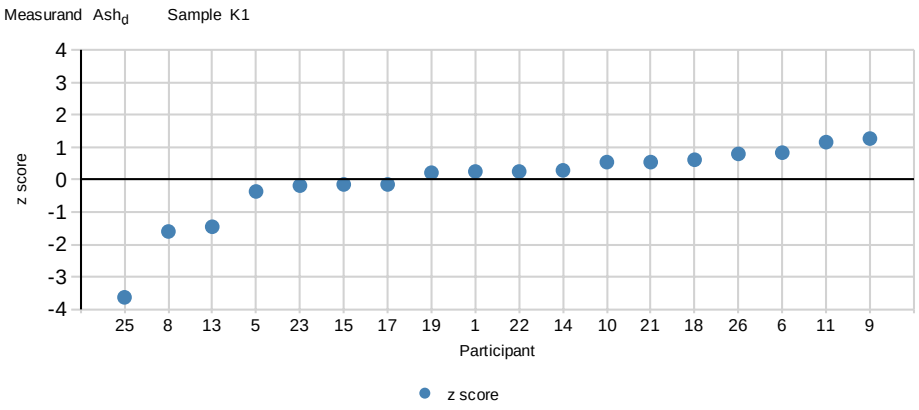
Measurand	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
C_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	-0.24	-0.12	.	.	-0.30	.	.	.	0.24	.	100
EF	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	-0.07	.	.	.	-0.05	.	.	.	-0.03	.	100
N_d	B1	.	.	.	.	.	.	.	.	.	.	.	.	.	0.04	-0.11	.	.	-0.91	.	.	.	0.35	.	100

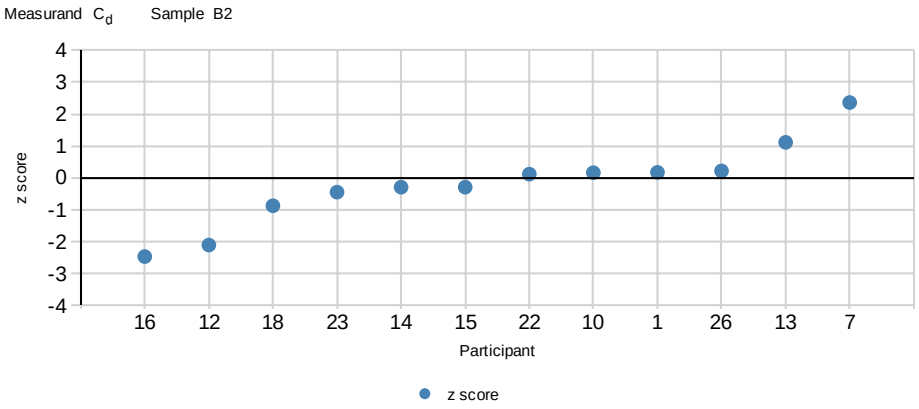
E_n scores enable to estimate the proximity of participant results to the assigned value taking into consideration their reported expanded uncertainty
Scores of $-1.0 < E_n < 1.0$ indicate successful performance
Scores of $E_n \geq 1.0$ or $E_n \leq -1.0$ indicate a need to review the uncertainty estimated or to correct a measurement issue

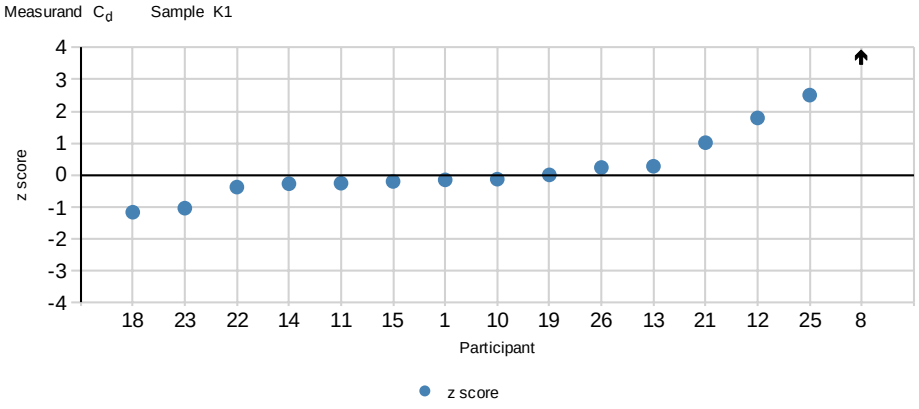
APPENDIX 10: z scores in ascending order

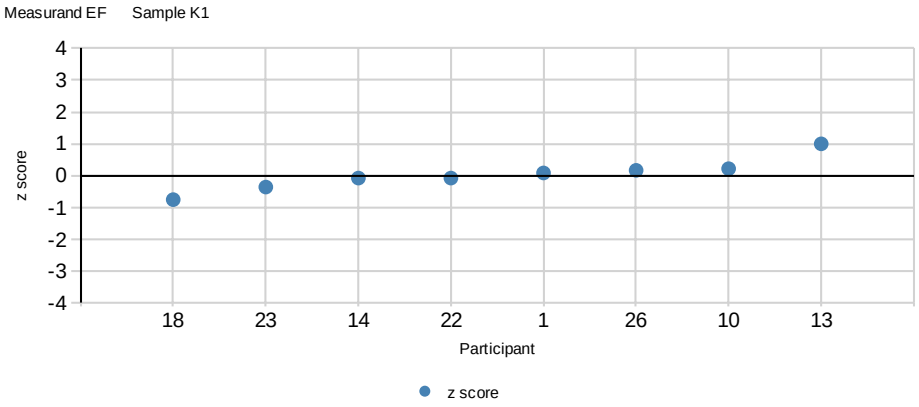


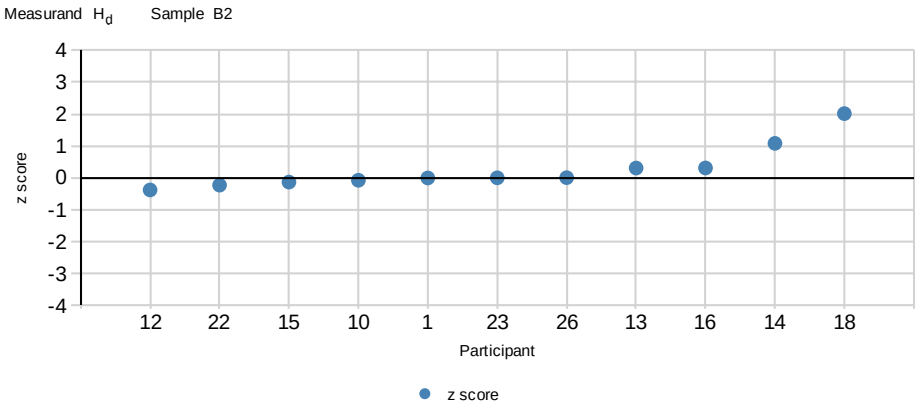


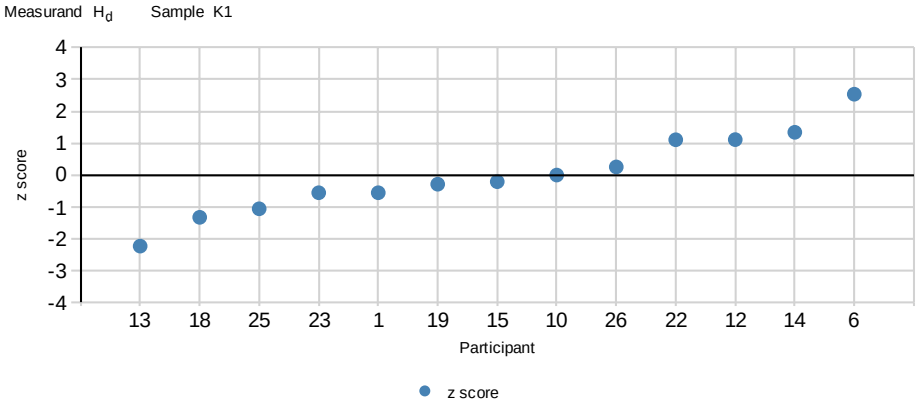


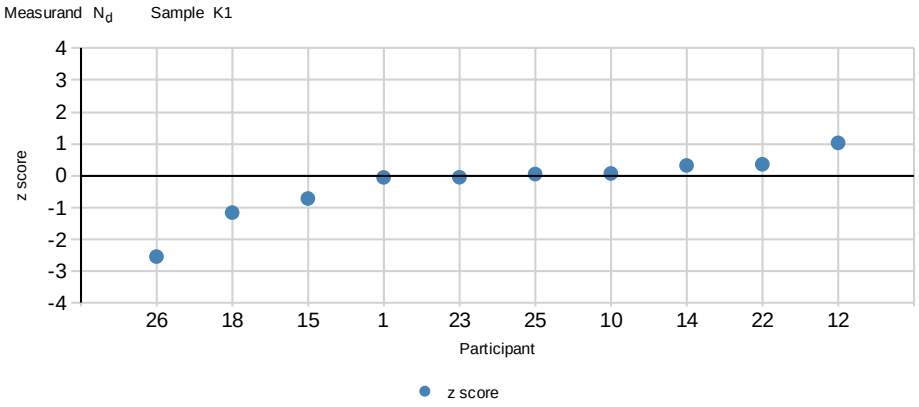

Measurand C_d Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
16 12 18 23 14 15 22 10 1 26 13 7
Participant
z score

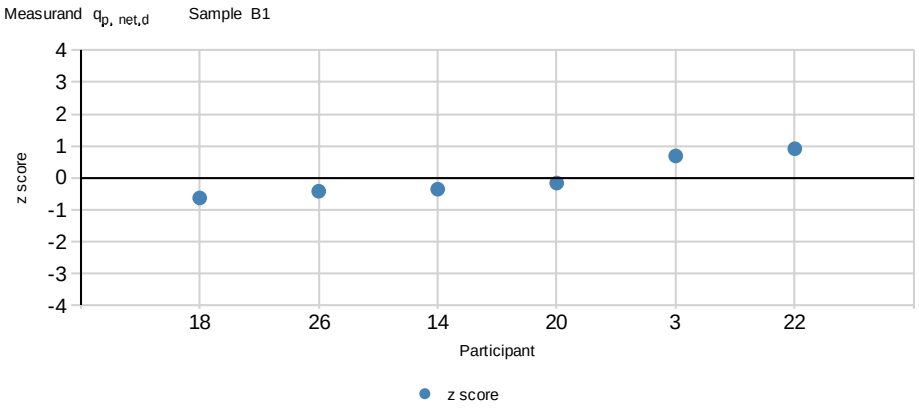

Measurand C_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
18 23 22 14 11 15 1 10 19 26 13 21 12 25 8
Participant
z score

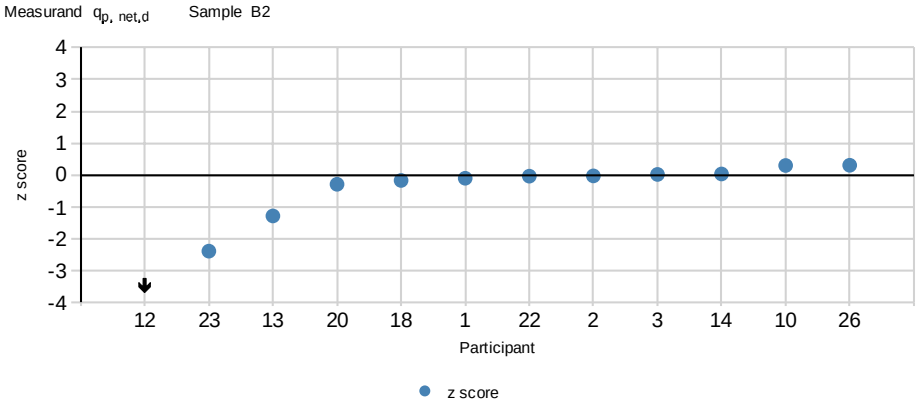

Measurand EF Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
18 23 14 22 1 26 10 13
Participant
z score

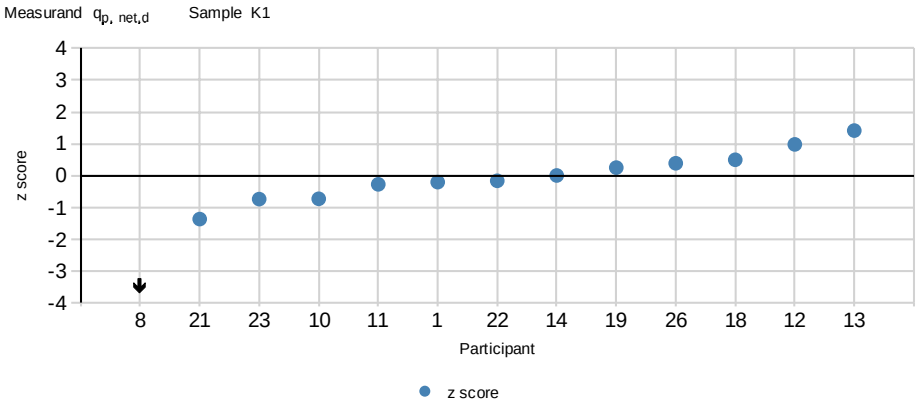

Measurand H_d Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
12 22 15 10 1 23 26 13 16 14 18
Participant
z score

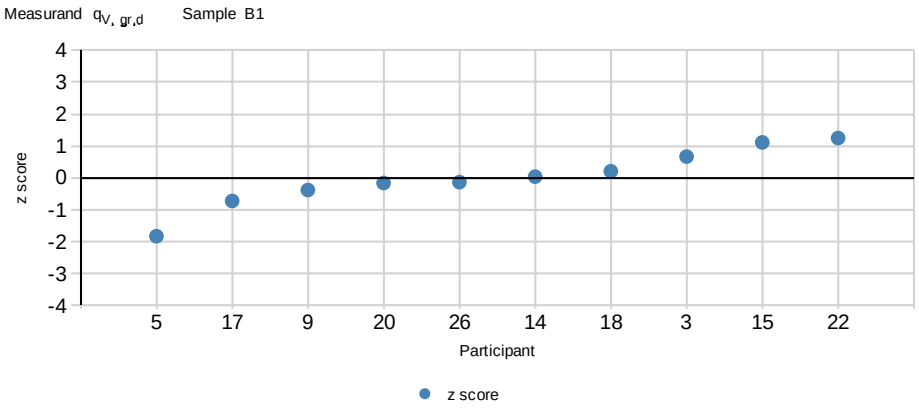

Measurand H_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
13 18 25 23 1 19 15 10 26 22 12 14 6
Participant
z score

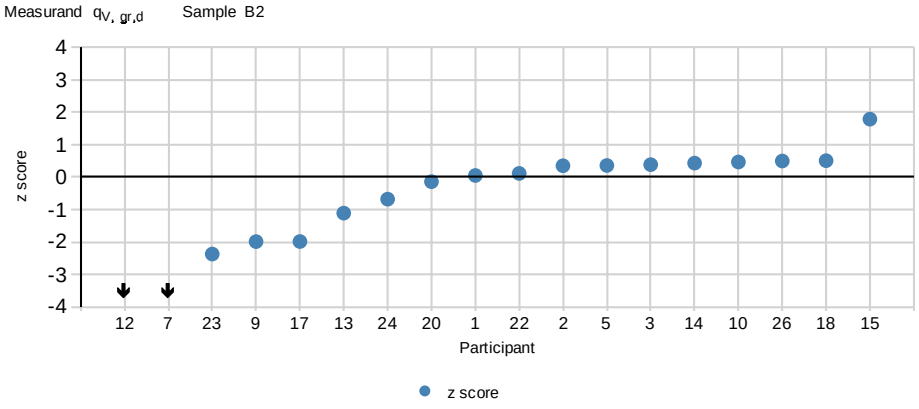

Measurand N_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
26 18 15 1 23 25 10 14 22 12
Participant
z score

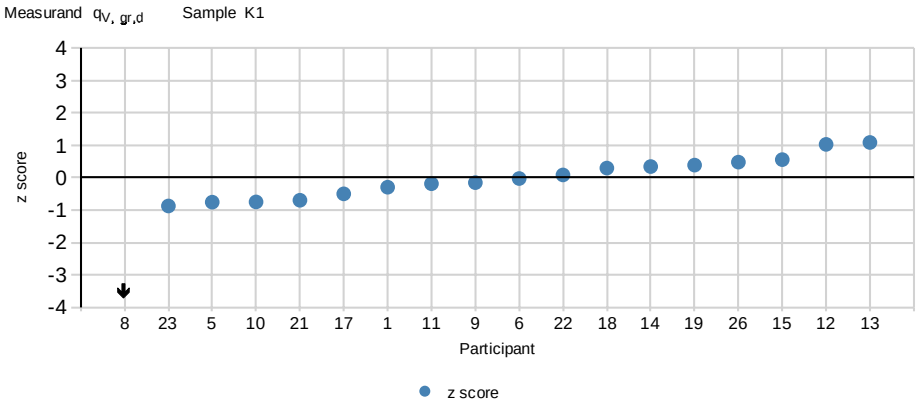

Measurand $q_{p,\,net,d}$ Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
18
26
14
20
3
22
Participant
z score

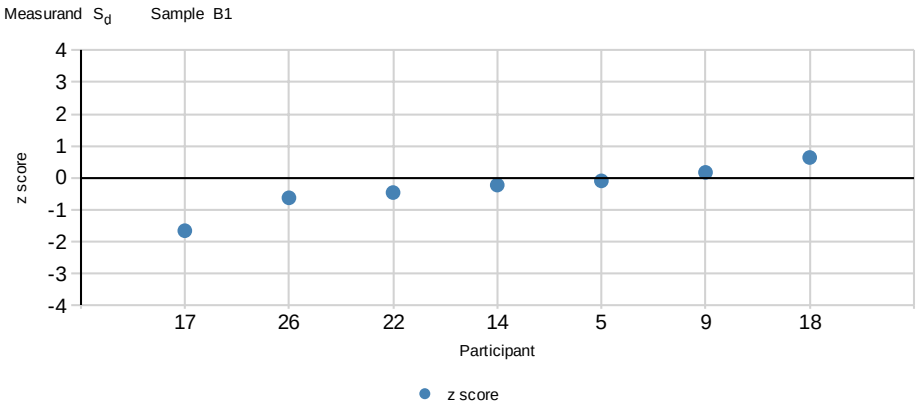

Measurand $q_{p,\,net,d}$ Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
12
23
13
20
18
1
22
2
3
14
10
26
Participant
z score

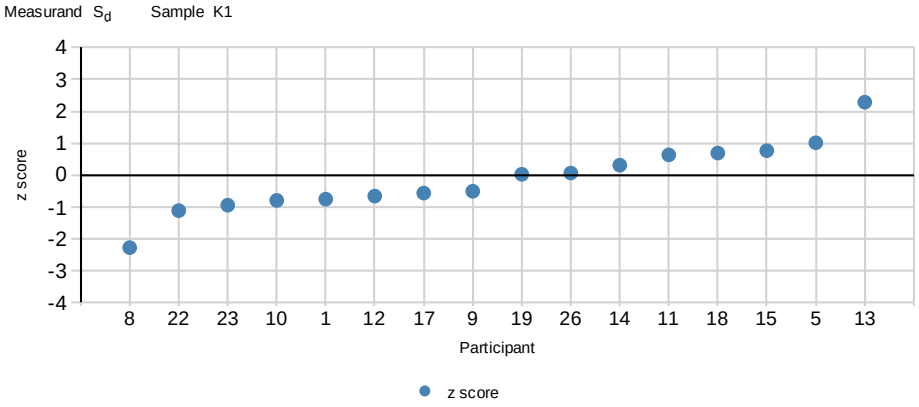

Measurand $q_{p,\,net,d}$ Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
8
21
23
10
11
1
22
14
19
26
18
12
13
Participant
z score

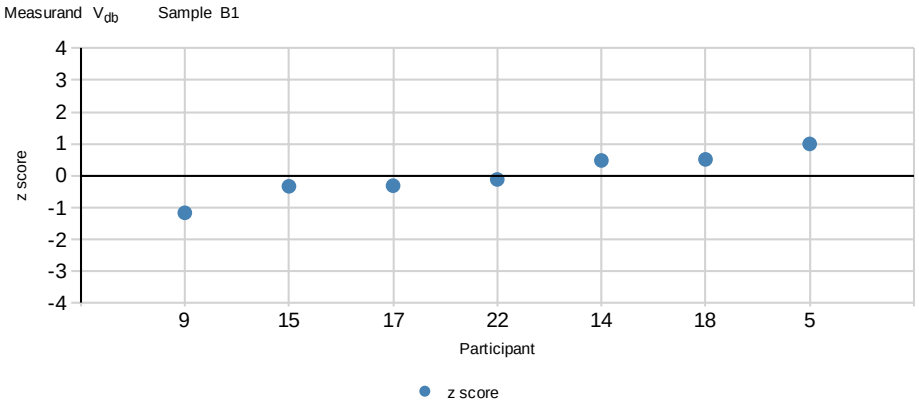

Measurand $q_{V,\ gr,d}$ Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
5 17 9 20 26 14 18 3 15 22
Participant
z score

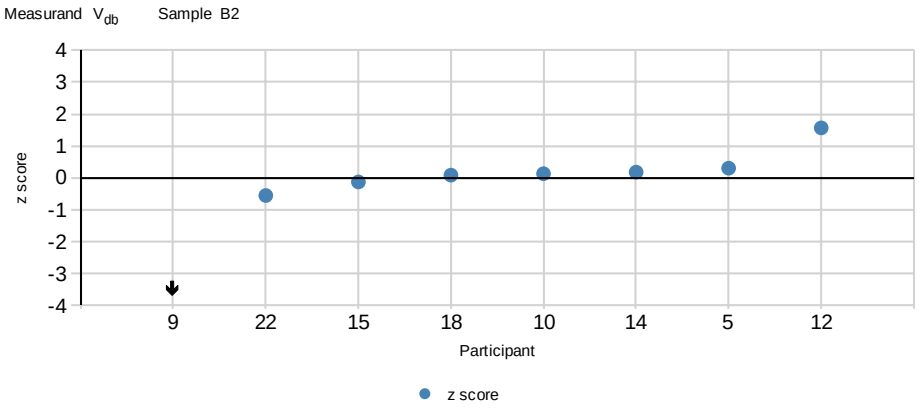

Measurand $q_{V,\ gr,d}$ Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
12 7 23 9 17 13 24 20 1 22 2 5 3 14 10 26 18 15
Participant
z score

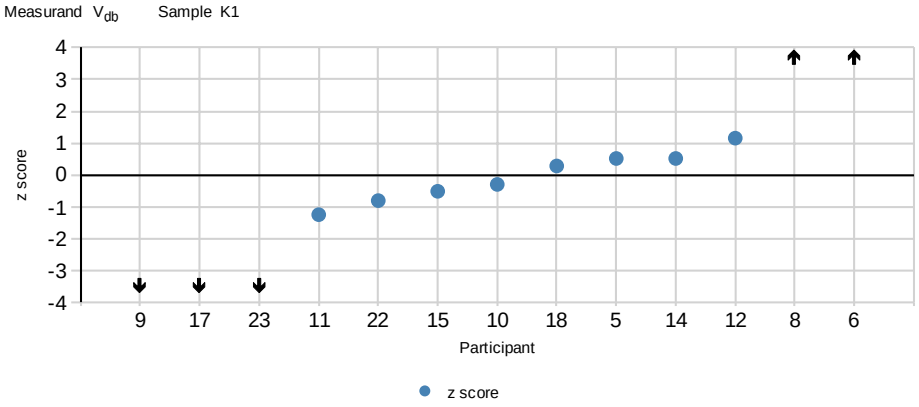

Measurand $q_{V,\ gr,d}$ Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
8 23 5 10 21 17 1 11 9 6 22 18 14 19 26 15 12 13
Participant
z score


Measurand S_d Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
17
26
22
14
5
9
18
Participant
z score


Measurand S_d Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
8
22
23
10
1
12
17
9
19
26
14
11
18
15
5
13
Participant
z score


Measurand V_{db} Sample B1
z score
4
3
2
1
0
-1
-2
-3
-4
9
15
17
22
14
18
5
Participant
z score


Measurand V_{db} Sample B2
z score
4
3
2
1
0
-1
-2
-3
-4
9
22
15
18
10
14
5
12
Participant
z score


Measurand V_{db} Sample K1
z score
4
3
2
1
0
-1
-2
-3
-4
9
17
23
11
22
15
10
18
5
14
12
8
6
Participant
z score

APPENDIX 11: Analytical measurements and background information for calculations

Reported details of the measurements:

Measurement of gross calorific value	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Air dried samples:	participants 9, 15, 18, 22	participants 1, 2, 9, 10, 13, 15, 16, 18, 22	participants 1, 9, 10, 13, 14, 15, 18, 19, 21, 22, 25
Drying in 105 °C:	participants 3, 14, 17	participants 3, 4, 12, 14, 17, 23, 24	participants 6, 8, 12, 17, 23
Other:	participant 4: 108°C, 5: not dried sample	participant 5: not dried sample	participant 5: not dried sample

Correction taken into account in calculations:

Gross calorific value			
Participants and correction factors used	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
1: wire, N, analysis moisture		x	
1: wire, S, N, analysis moisture			x
2: ignition, S, N, acid correction, analysis moisture		x	
3: wire, ignition, acid correction	x	x	
5: wire, S, N, analysis moisture	x	x	x
6: S, acid correction, analysis moisture			x
8: S			x
9: wire, S, analysis moisture	x		
9: wire, analysis moisture		x	
9: wire, S, N, analysis moisture			x
10: ignition, S, N, analysis moisture		x	x
12: wire, S, N		x	x
13: wire, S, acid correction		x	x
14: wire, S, acid correction	x	x	
14: wire, S, acid correction, analysis moisture			x
15: wire, ignition, S, N, acid correction, analysis moisture	x	x	x
17: wire, ignition, acid correction, analysis moisture	x	x	x
18: wire, ignition, S, N, acid correction, analysis moisture	x		x
18: wire, ignition, N, acid correction, analysis moisture		x	
19: wire, ignition, S, acid correction, analysis moisture			x
21: wire, ignition, analysis moisture			x
22: wire, ignition, acid correction, analysis moisture	x	x	x
23: wire, ignition, S, N, acid correction		x	x
24: wire, acid correction, analysis moisture		x	

Correction taken into account in calculations:

Net calorific value (literature value in brackets)			
Participant	Sample		
	B1 (peat)	B2 (wood pellet)	K1 (coal)
1		N+O, H	N+O, H
2		N+O (42 % + 0.2 %) H (6.2 %)	
3	N+O, H	N+O, H	
8			H (3.78)
10		O, N+O, H	O, N+O, H
12		H	H
13		N+O, H	N+O, H
14	N+O, H	N+O, H	N+O, H
15	H	H	H
18	N+O, H	N+O, H	N+O, H
19			H
21			H calculated (4.89)
22	N+O, H	N+O, H	N+O, H
23		N+O, H	N+O, H
25			H calculated (49.22)

Methods used in ash and moisture measurements:

Measurement	Method	°C	Sample B1 (peat)	Sample B2 (wood pellet)	Sample K1 (coal)
Ash content (ashing temperature ℃)	Gravimetric	500		part 13	
		550	parts 3, 5, 18, 22	parts 1, 2, 3, 4, 5, 10, 15, 22	
		815	parts 4, 15, 17	part 23	parts 1, 5, 6, 10, 13, 15, 17, 18, 21, 22, 23
		850		part 17	part 8
		950		part 12	part 12
	TGA:	550	parts 9, 14	parts 9, 14	
		750			part 19
		815	part 15		parts 9, 14, 15, 25
	Other: GUM			part 24	
Moisture content of analysis sample, M_{ad} (temperature °C)	Air:		parts 3, 4, 5, 9, 14, 17, 18, 22	parts 1, 2,3, 4, 5, 9, 10, 12, 13,14, 16, 17, 18, 22, 23	parts 1, 5, 6, 8, 9, 10, 13, 17, 21, 23
	N_2 atmosphere:		part 15	part 15	parts 12, 15, 19, 25
	Gravimetric:	105	parts 3, 5, 17, 18, 22	parts 1, 2, 3, 4, 5, 10, 12, 13, 16, 17, 18, 22, 23	parts 1, 5, 6, 8, 10, 12, 13, 17, 18 19, 21, 23
		107.5			part 22
		108	part 4		
	TGA:	105	parts 9, 14, 15	parts 9, 14, 15	parts 9, 14, 15
	Other:	>107			part 25
Relative humidity of analyzing room (%)	part 1: 37, part 2: 72, part 3: 51, part 5: 39, part 6: 49, part 9: 59, part 12: 30, part 13: 38, part 16: 60, part 18: 45, part 19: 27, part 21: 55, part 22: 34, part 23: 59, part 24: 38				

CHN-measurements carried out by:

Sample			
	B1	B2	K1
Air dried samples:	parts 14, 15, 22	parts 1, 10, 13, 14, 15, 22	parts 1, 10, 13, 14, 15, 18,19, 21, 22, 25
Drying in 105 °C:	part 18	parts 12, 16, 18, 23	parts 8, 12, 23

Detection limits in nitrogen and sulphur measurements:

Participant	Detection limit for N (w%)	Participant	Detection limit for S (w%)
1	0.02	1	0.05
12	1	8	10
15	1	12	1
18	0,1	13	1
22	0.03	15	1
22	0.03	18	0.03
		22	0.002

Calculations of Emission factor (EF)[1]:

We have used the equation based on the decision EU601/2012(21.6.2012).
If no, describe how?

	Sample B1 (peat)	Sample K1 (coal)
Yes:	parts 14, 15, 18, 22	parts 1, 10, 13, 14, 15, 18, 22, 23
No:		parts 8, 19, 25

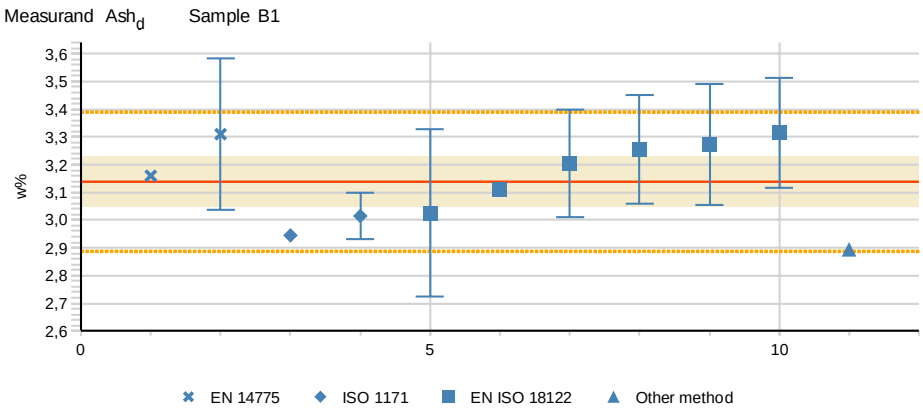
[1]In the cover letter the provider gave the participants the possibility to calculate the EF-value using the procedure presented in the EC directive and using the total moisture content as presented in the letter. Later it was obtained, that the EC directive is not giving the detailed equation for calculation of EF-values. Therefore, some national guides for the equation of EF value calculation have been produced.
As a result from this, the Energy Market Authority in Finland has made the guideline for the calculation of emission factor for fossile fuels as follows:

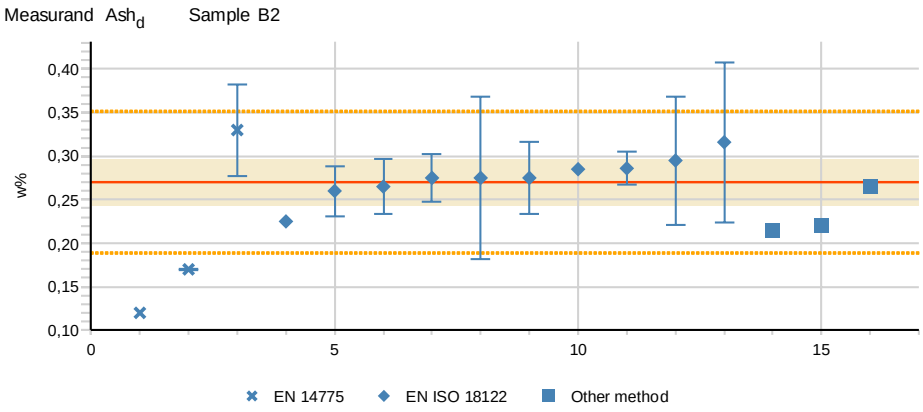
$EF = 1000 \times 3.664 \times (C/100) \times (1 - M_{ar}/100)/Q_{net.ar}$, where

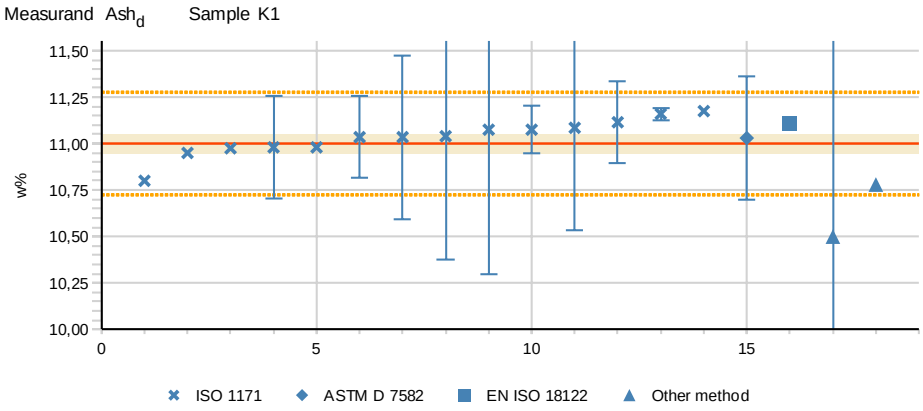
EF emission factor, g CO_2/MJ
C carbon content as dry, %
M_{ar} total moisture as received, %
$Q_{net.ar}$ net calorific value as received, MJ/kg
(http://www.energiavirasto.fi/documents/10179/132665/Paastokertoimen+laskentaohje.pdf)

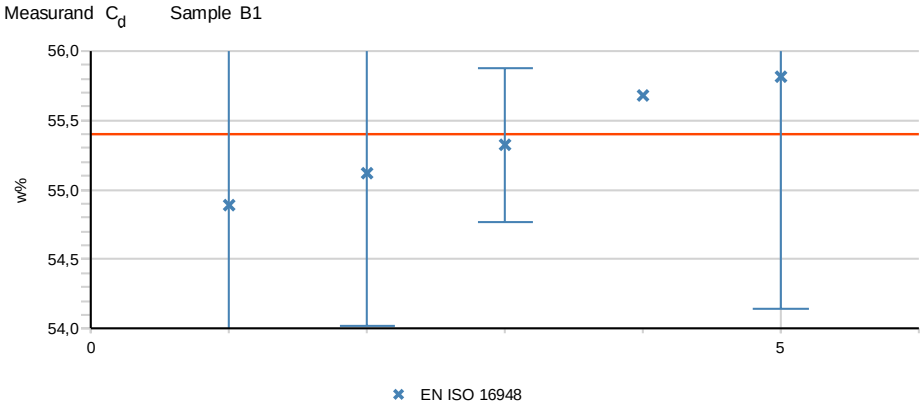
APPENDIX 12: Results grouped according to the methods

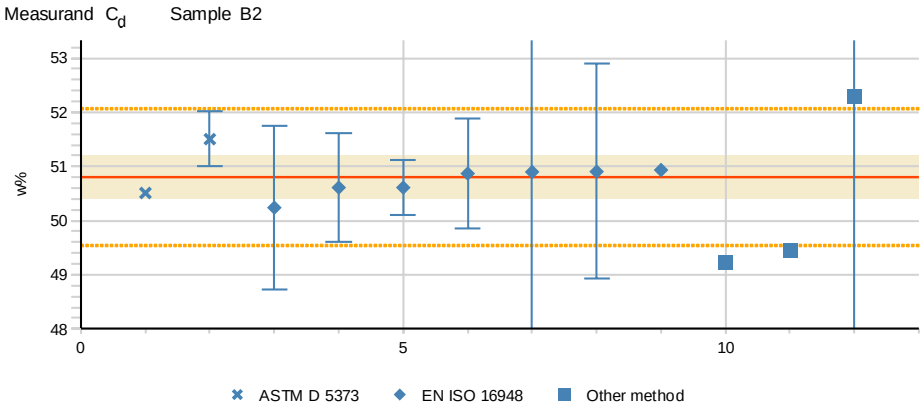
The explanations for the figures are described in the Appendix 9. The results are shown in ascending order.

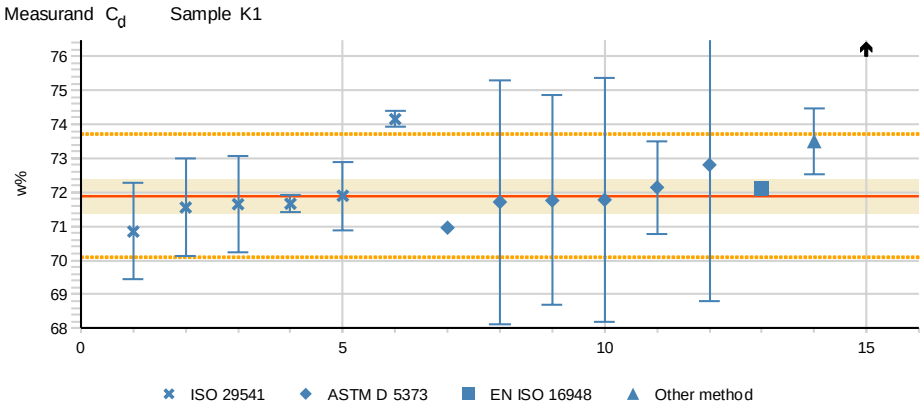




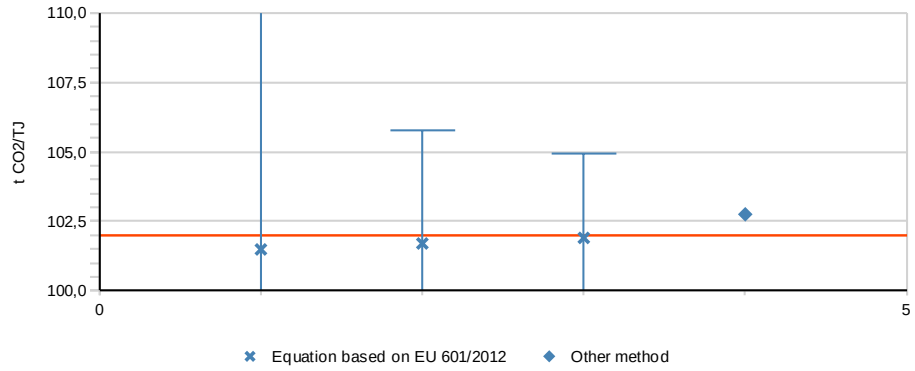



Measurand C_d Sample B1
56,0
55,5
55,0
54,5
54,0
w%
0
5
EN ISO 16948

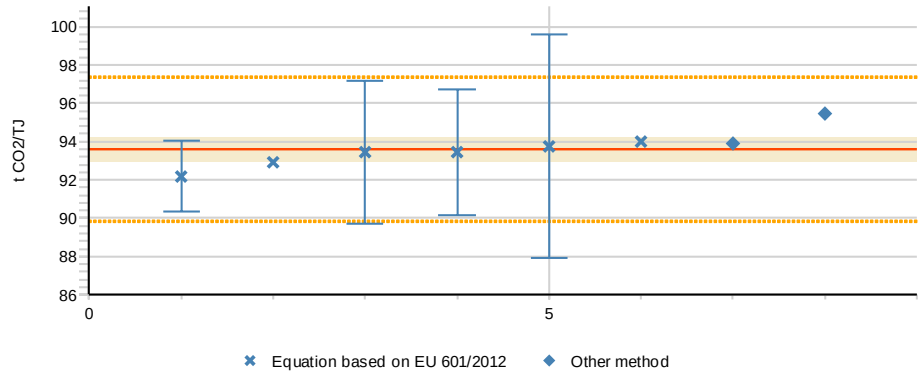

Measurand C_d Sample B2
53
52
51
50
49
48
w%
0
5
10
ASTM D 5373
EN ISO 16948
Other method


Measurand C_d Sample K1
76
75
74
73
72
71
70
69
68
w%
0
5
10
15
ISO 29541
ASTM D 5373
EN ISO 16948
Other method

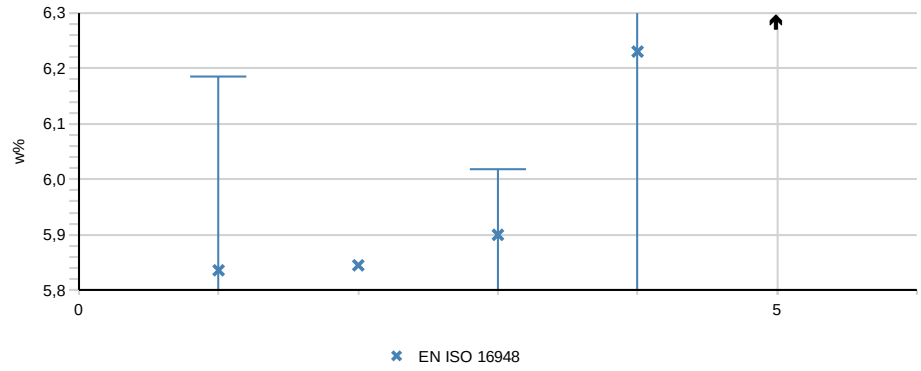
Measurand EF Sample B1

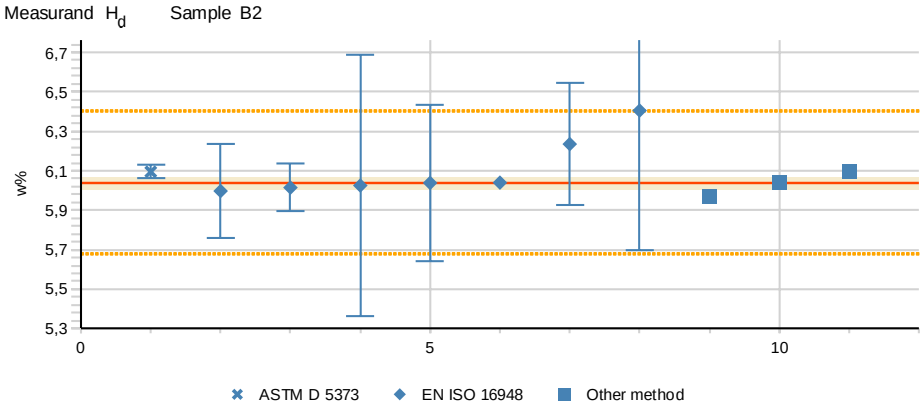


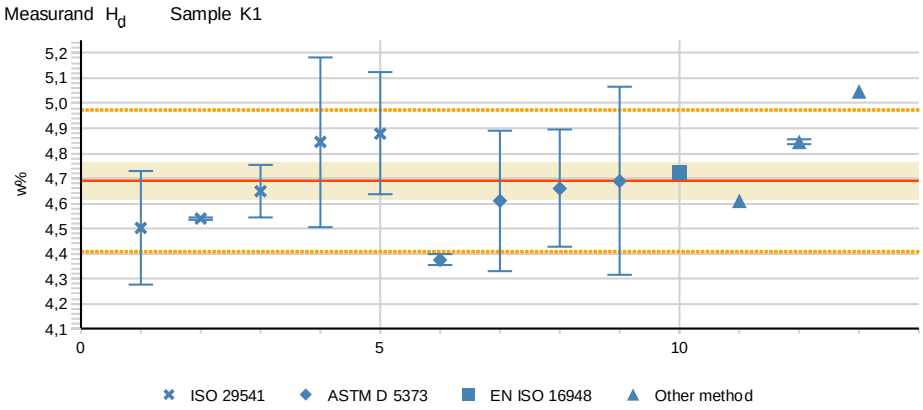
Measurand EF Sample K1

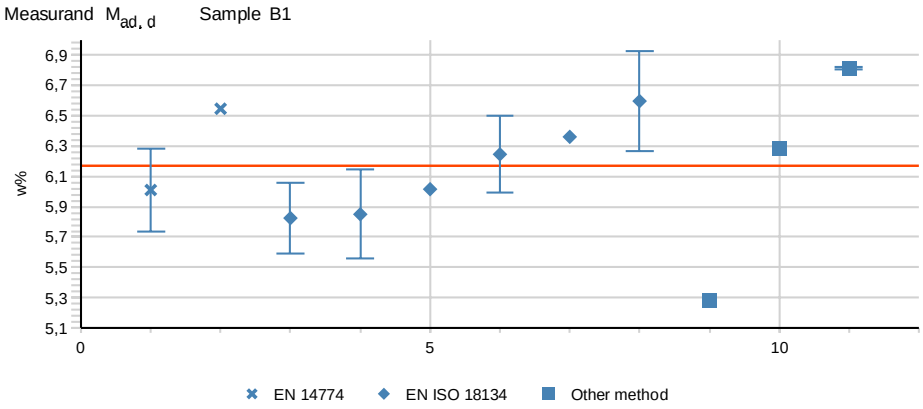


Measurand H_d Sample B1

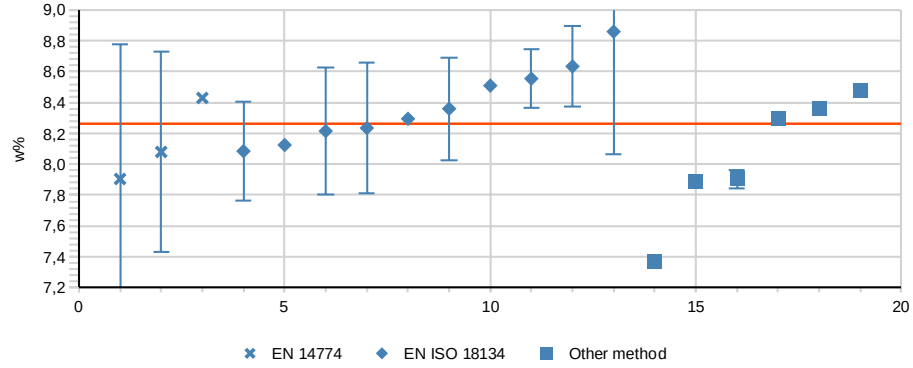



Measurand H_d Sample B2
w%
6,7
6,5
6,3
6,1
5,9
5,7
5,5
5,3
0
5
10
ASTM D 5373
EN ISO 16948
Other method

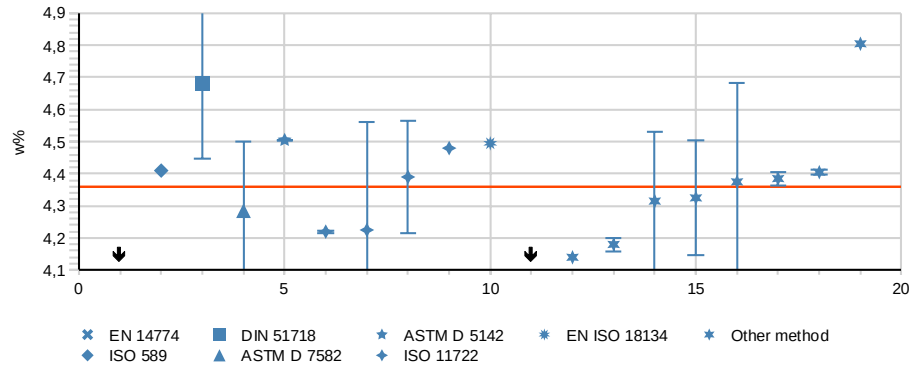

Measurand H_d Sample K1
w%
5,2
5,1
5,0
4,9
4,8
4,7
4,6
4,5
4,4
4,3
4,2
4,1
0
5
10
ISO 29541
ASTM D 5373
EN ISO 16948
Other method


Measurand $M_{ad,d}$ Sample B1
w%
6,9
6,7
6,5
6,3
6,1
5,9
5,7
5,5
5,3
5,1
0
5
10
EN 14774
EN ISO 18134
Other method

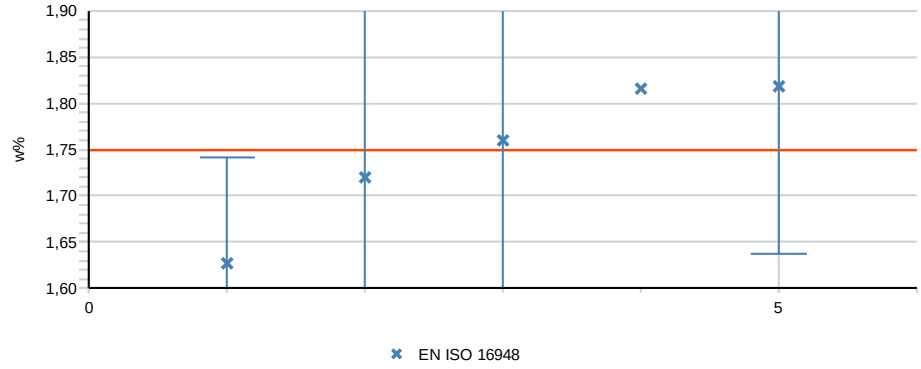
Measurand $M_{ad,d}$ Sample B2

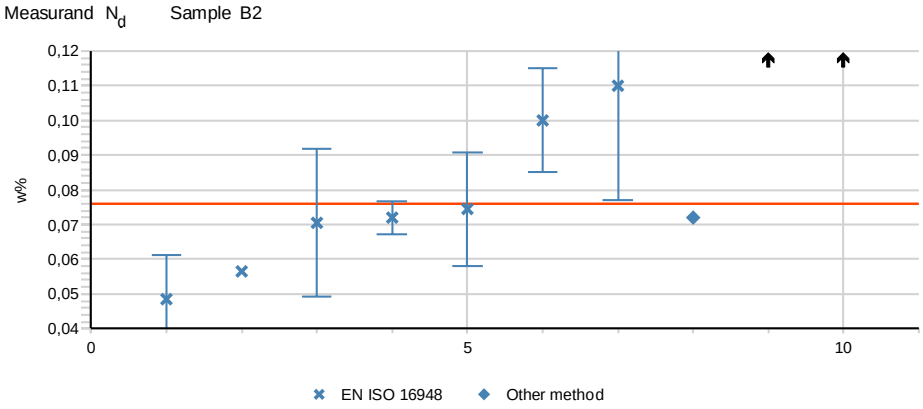


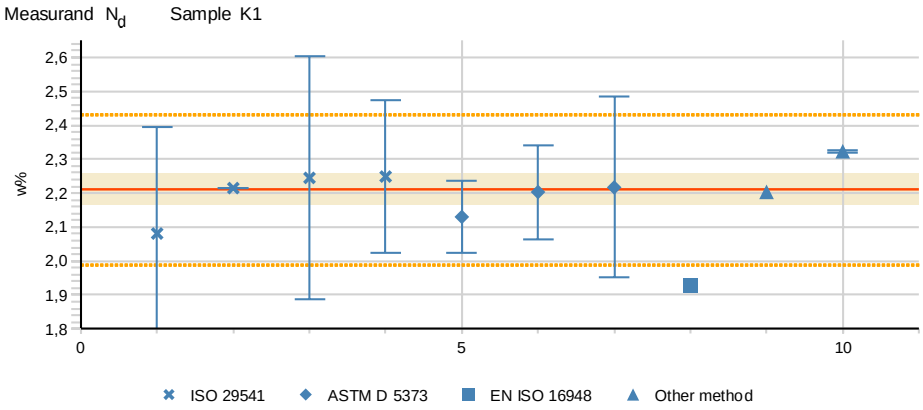
Measurand $M_{ad,d}$ Sample K1

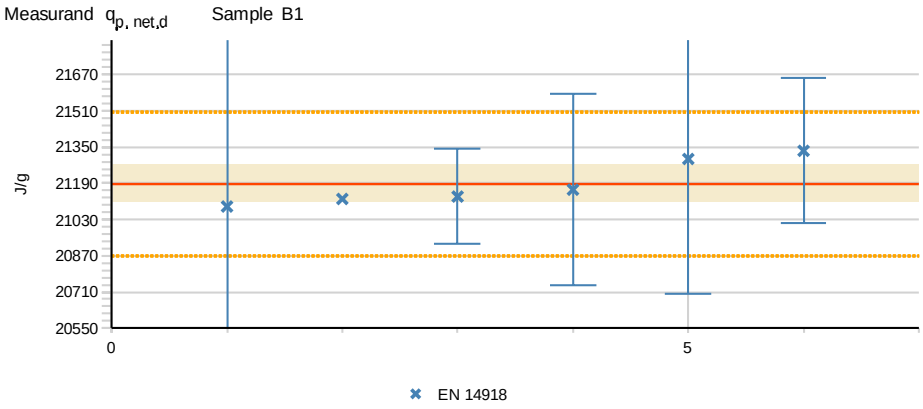


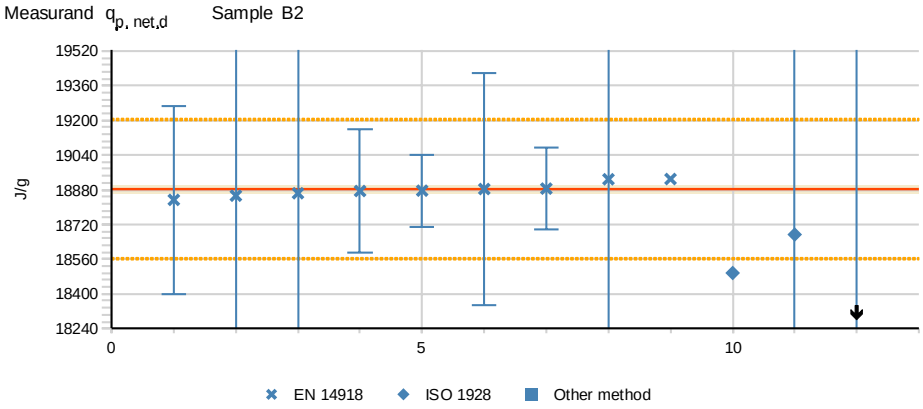
Measurand N_d Sample B1

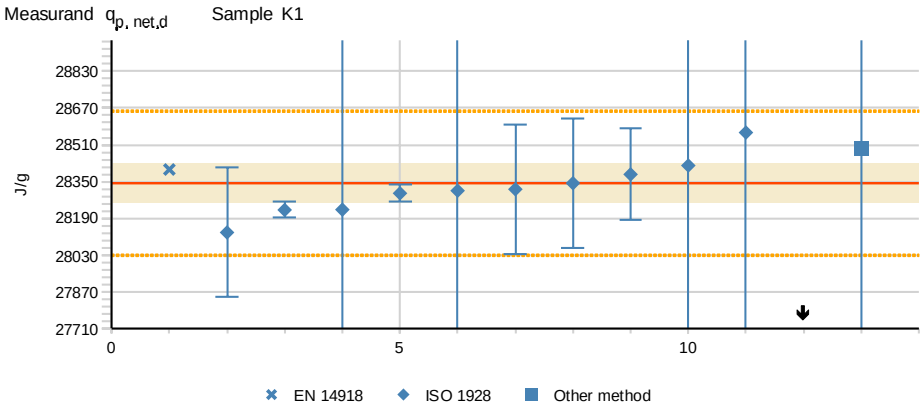


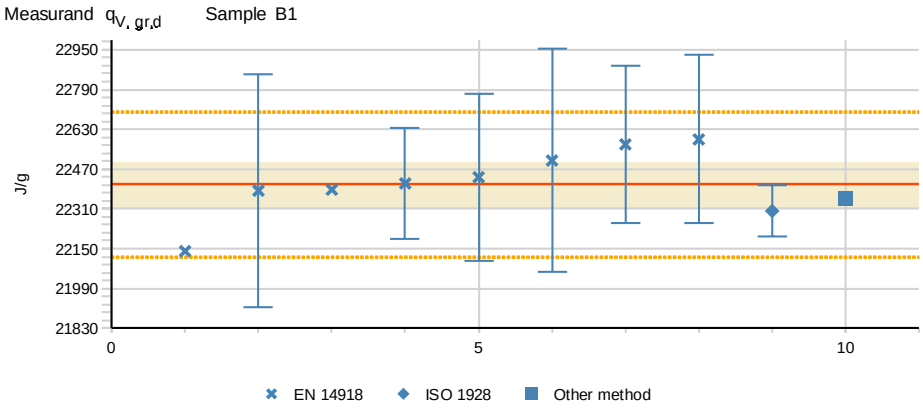

Measurand N_d Sample B2
w%
0,12
0,11
0,10
0,09
0,08
0,07
0,06
0,05
0,04
0
5
10
EN ISO 16948
Other method

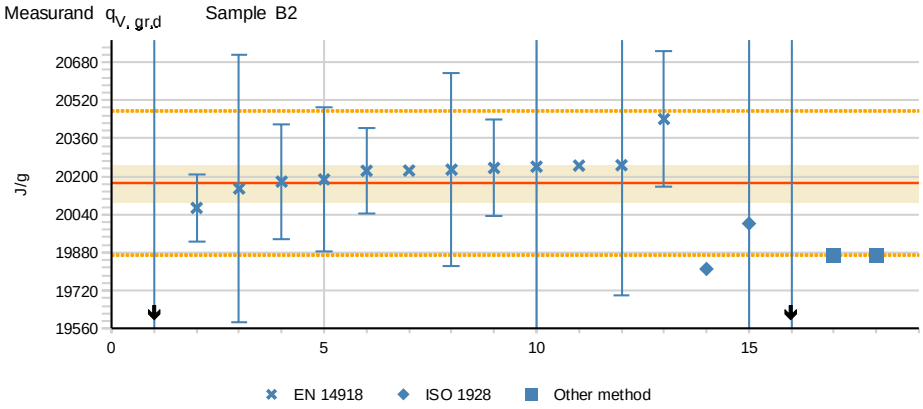

Measurand N_d Sample K1
w%
2,6
2,5
2,4
2,3
2,2
2,1
2,0
1,9
1,8
0
5
10
ISO 29541
ASTM D 5373
EN ISO 16948
Other method

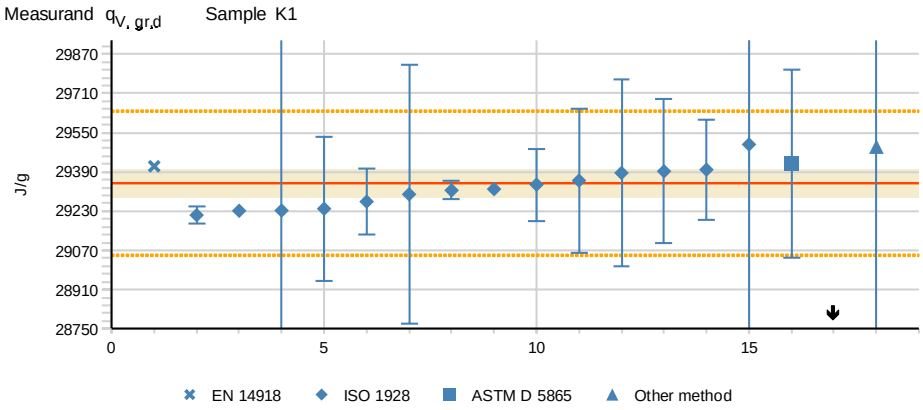

Measurand $q_{p,\,net,d}$ Sample B1
J/g
21670
21510
21350
21190
21030
20870
20710
20550
0
5
EN 14918

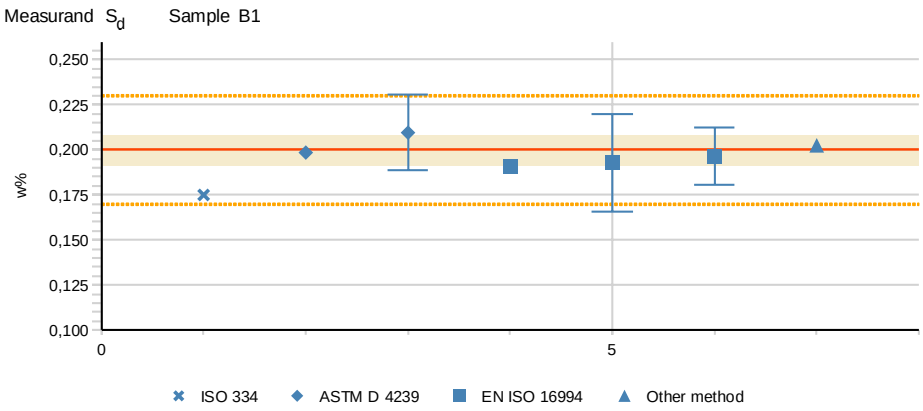

Measurand $q_{p,\ net,d}$
Sample B2
J/g
19520
19360
19200
19040
18880
18720
18560
18400
18240
0
5
10
EN 14918
ISO 1928
Other method


Measurand $q_{p,\ net,d}$
Sample K1
J/g
28830
28670
28510
28350
28190
28030
27870
27710
0
5
10
EN 14918
ISO 1928
Other method

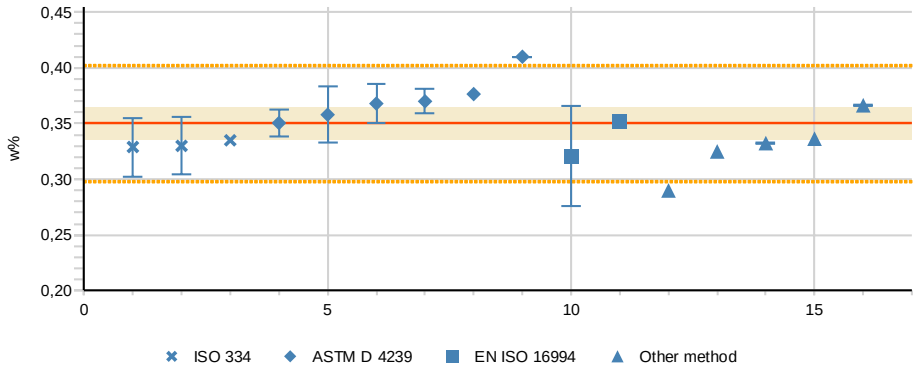

Measurand $q_{V,\ gr,d}$
Sample B1
J/g
22950
22790
22630
22470
22310
22150
21990
21830
0
5
10
EN 14918
ISO 1928
Other method


Measurand $q_{V, gr,d}$ Sample B2
J/g
20680
20520
20360
20200
20040
19880
19720
19560
0
5
10
15
EN 14918
ISO 1928
Other method

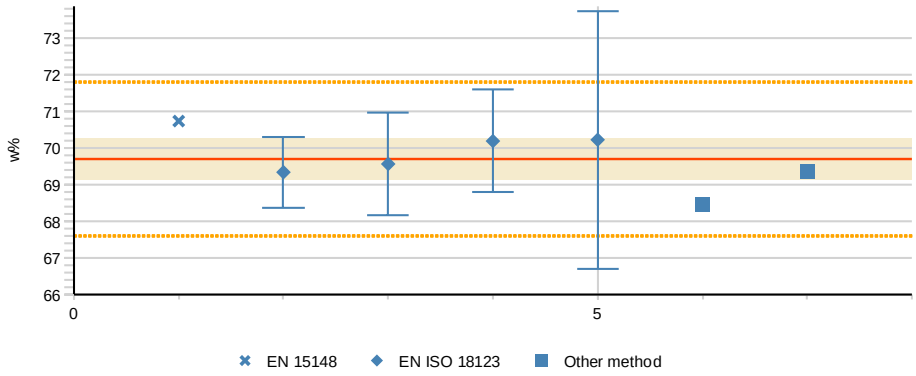

Measurand $q_{V, gr,d}$ Sample K1
J/g
29870
29710
29550
29390
29230
29070
28910
28750
0
5
10
15
EN 14918
ISO 1928
ASTM D 5865
Other method


Measurand S_d Sample B1
w%
0,250
0,225
0,200
0,175
0,150
0,125
0,100
0
5
ISO 334
ASTM D 4239
EN ISO 16994
Other method

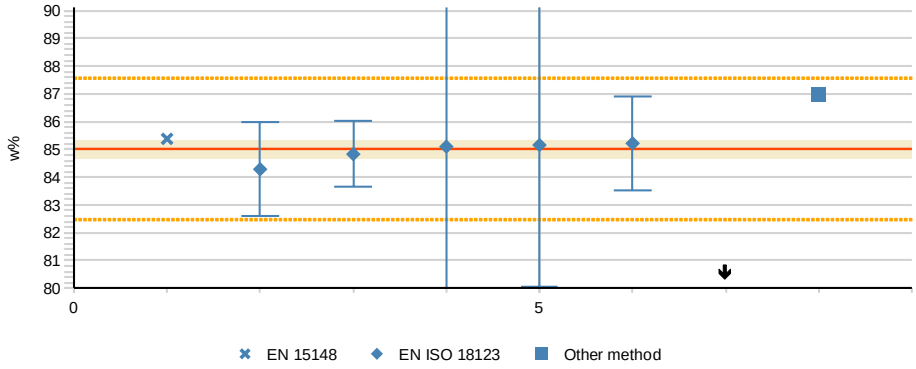
Measurand S_d Sample K1

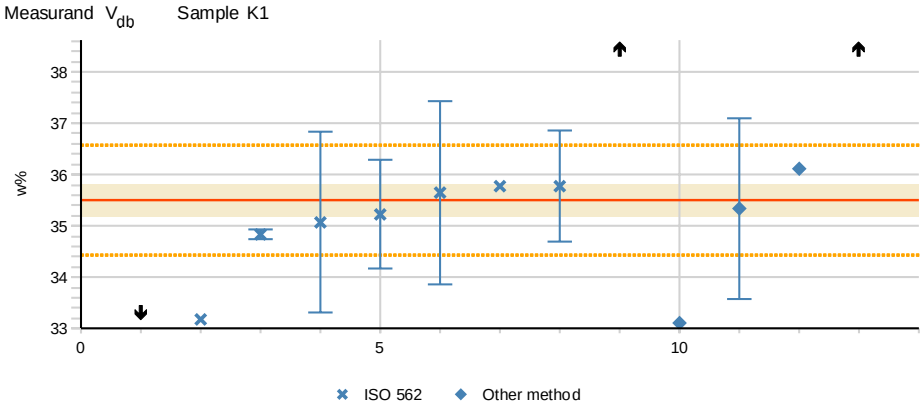


Measurand V_{db} Sample B1



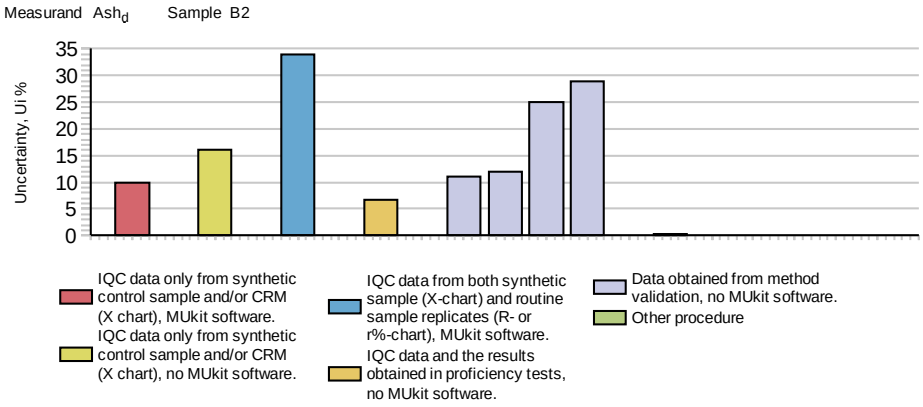
Measurand V_{db} Sample B2

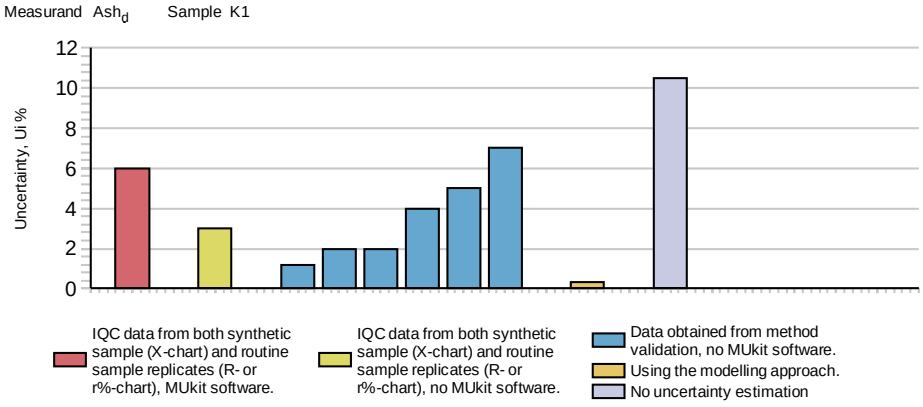


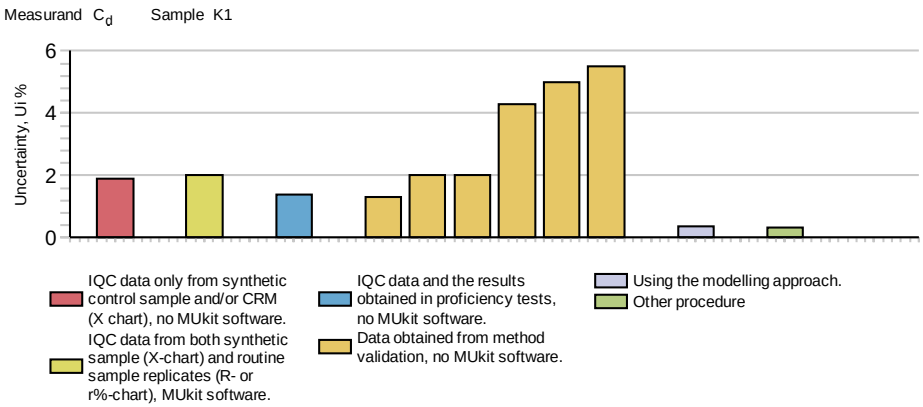

Measurand V_{db}
Sample K1
w%
38
37
36
35
34
33
0
5
10
ISO 562
Other method

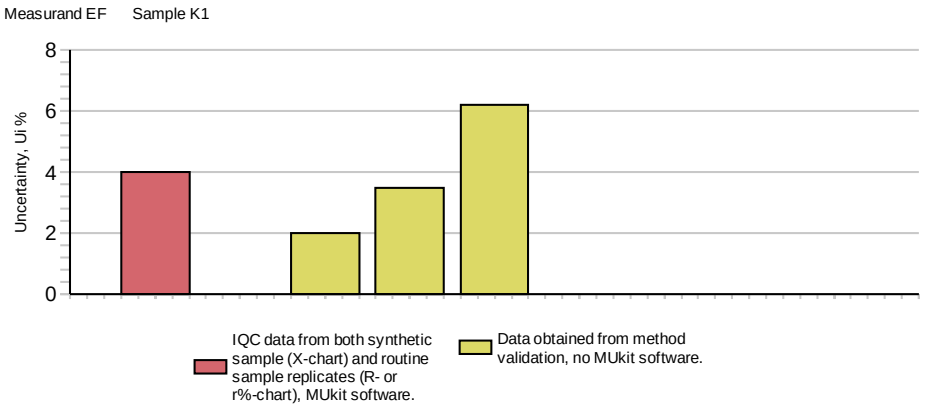
APPENDIX 13: Examples of measurement uncertainties reported by the participants

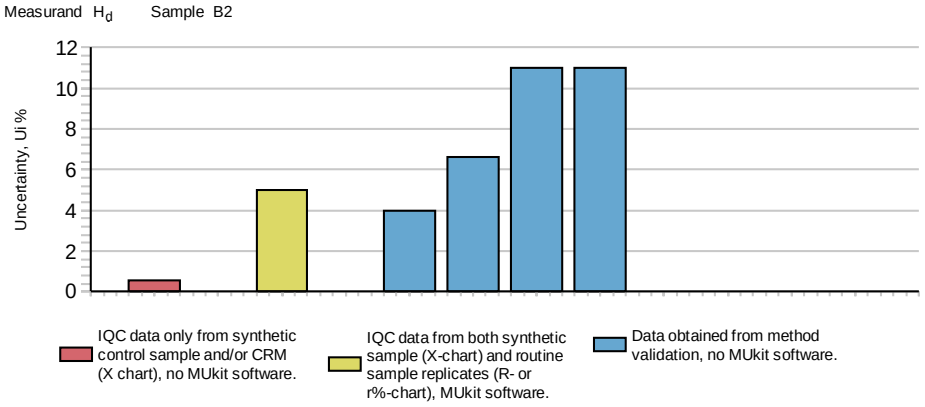
In figures, the presented expanded measurement uncertainties are grouped according to the method of estimation at 95 % confidence level (k=2). The expanded uncertainties were estimated mainly by using the internal quality control (IQC) data. The used procedures in figures below are distinguished e.g. between using or not using the MUkit software for uncertainty estimation [27, 28] or using a modelling approach based [29, 30].

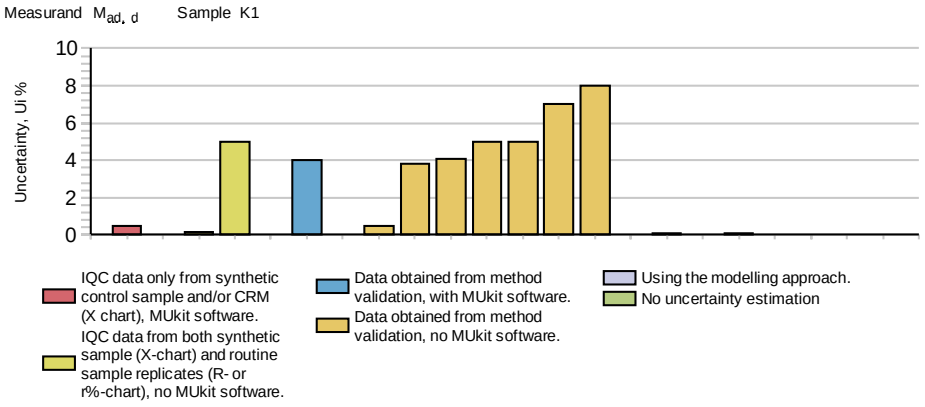


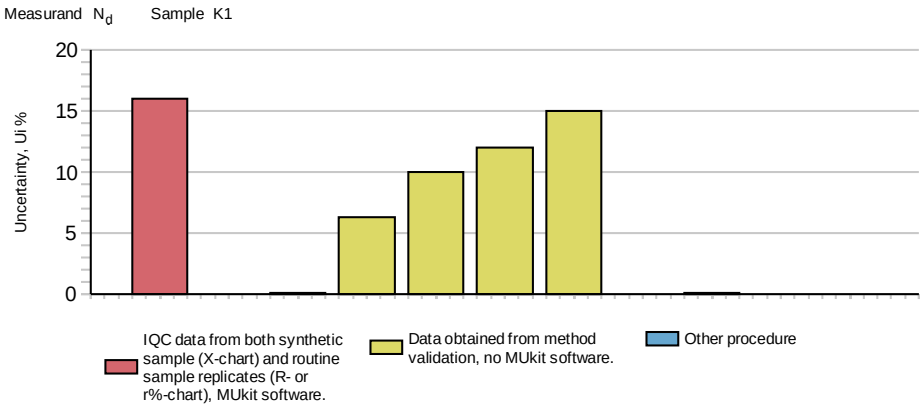


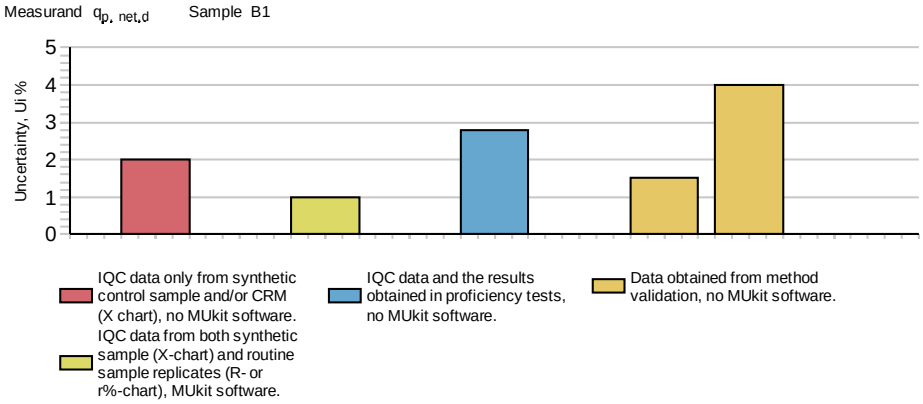


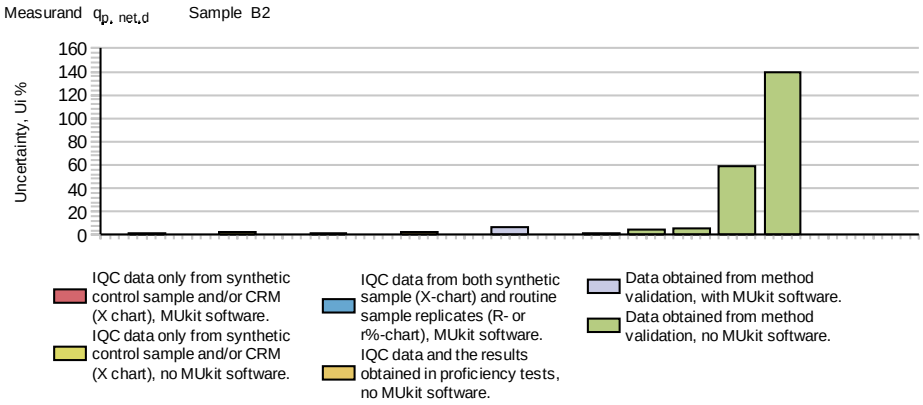

Measurand EF Sample K1
Uncertainty, Ui %
0
2
4
6
8
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.

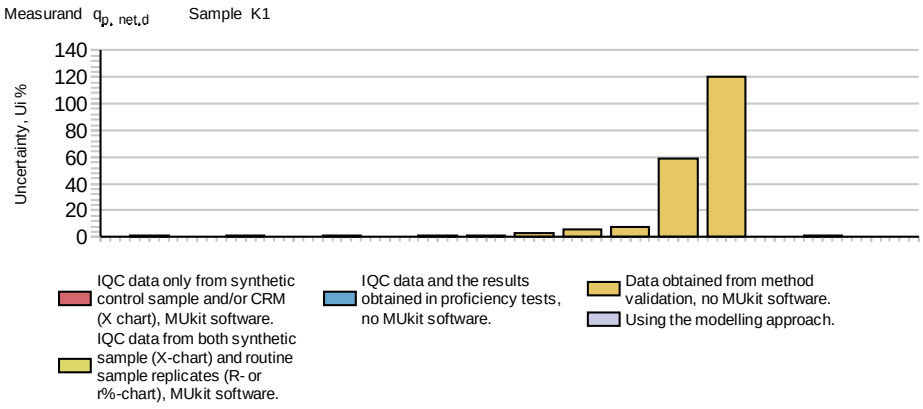

Measurand H_d Sample B2
Uncertainty, Ui %
0
2
4
6
8
10
12
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.

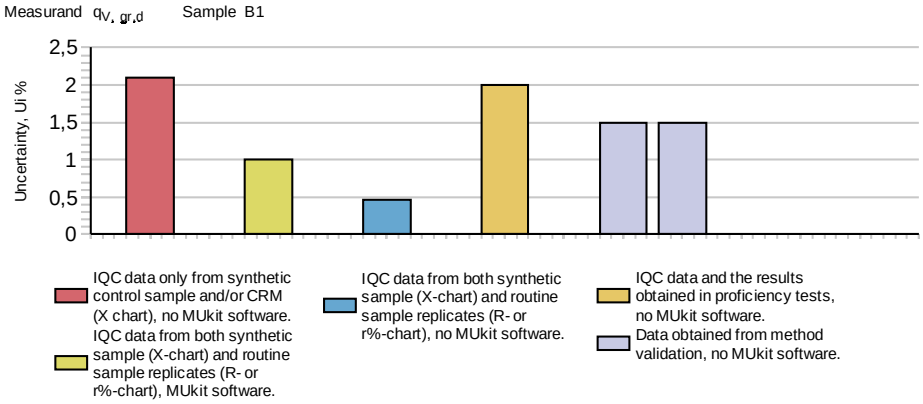

Measurand $M_{ad,\ d}$ Sample K1
Uncertainty, Ui %
0
2
4
6
8
10
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
No uncertainty estimation

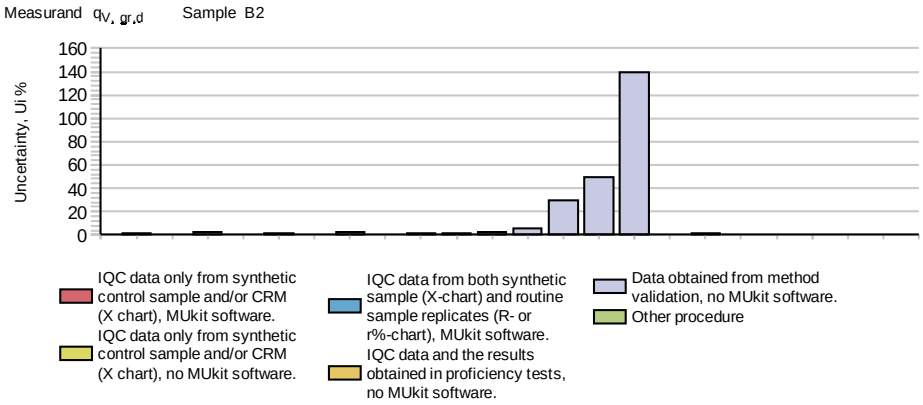

Measurand N_d Sample K1
Uncertainty, Ui %
20
15
10
5
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure

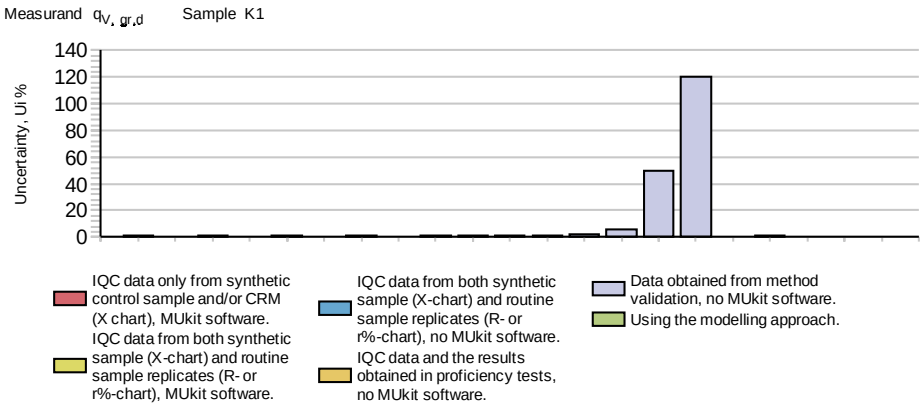

Measurand $q_{p,\,net,d}$ Sample B1
Uncertainty, Ui %
5
4
3
2
1
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.

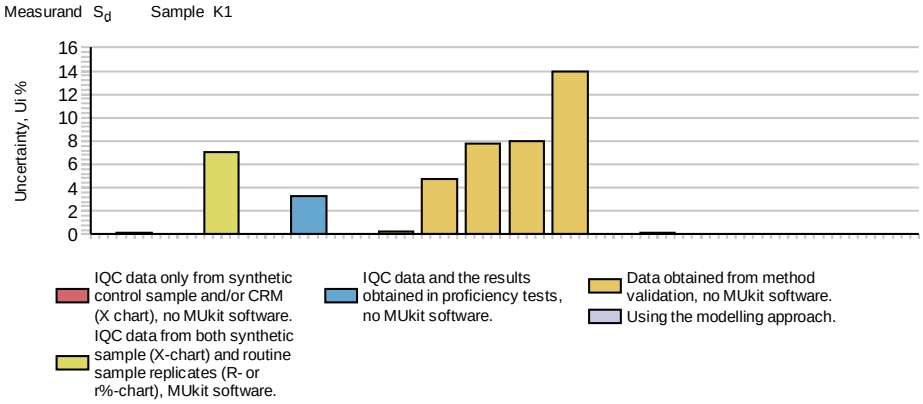

Measurand $q_{p,\,net,d}$ Sample B2
Uncertainty, Ui %
160
140
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, with MUkit software.
Data obtained from method validation, no MUkit software.
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.

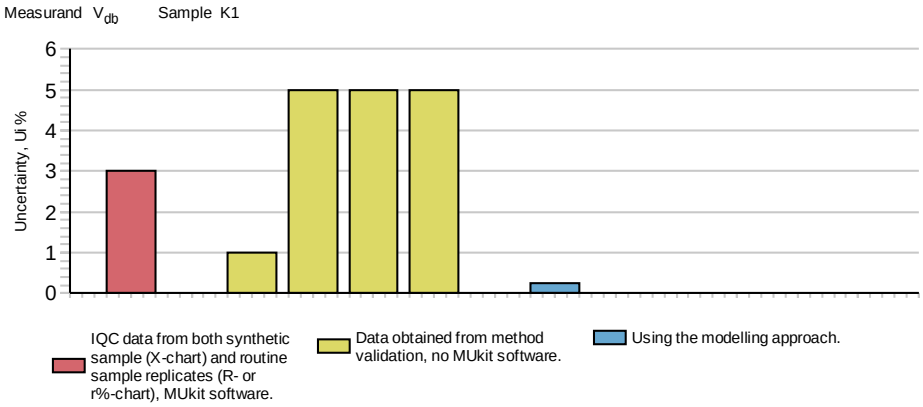

Measurand $q_{p,\ net,d}$ Sample K1
Uncertainty, Ui %
140
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.


Measurand $q_{V,\ gr,d}$ Sample B1
Uncertainty, Ui %
2,5
2
1,5
1
0,5
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.


Measurand $q_{V,\ gr,d}$ Sample B2
Uncertainty, Ui %
160
140
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.
Other procedure
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.


Measurand $q_{V,gr,d}$ Sample K1
Uncertainty, Ui %
140
120
100
80
60
40
20
0
IQC data only from synthetic control sample and/or CRM (X chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), no MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand S_d Sample K1
Uncertainty, Ui %
16
14
12
10
8
6
4
2
0
IQC data only from synthetic control sample and/or CRM (X chart), no MUkit software.
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
IQC data and the results obtained in proficiency tests, no MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.


Measurand V_{db} Sample K1
Uncertainty, Ui %
6
5
4
3
2
1
0
IQC data from both synthetic sample (X-chart) and routine sample replicates (R- or r%-chart), MUkit software.
Data obtained from method validation, no MUkit software.
Using the modelling approach.

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